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Possibilities for optimization of technological modes for ethylene polymerization in autoclave and tubular reactors

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Abstract

Results of experimental studies on high-pressure ethylene polymerization in industrial autoclave and tubular reactors are considered using various peroxides and their mixtures with oxygen as initiators.

A possibility for the process improvement providing the increase of conversion, productivity and versatility of the obtained polyethylene brands is demonstrated.

According to the experimental data for the processes performed in single- and double-zone mixing mode reactors the initiator consumption, temperature profile stability and possibilities for rapid control over the process are analyzed depending on the type of the used peroxides or their complex mixtures.

Peculiarities of ethylene polymerizations in tubular reactors using the initiators either individually (stepwise initiation) or in a complex (mixed) initiation mode are revealed and discussed.

Keywords: Autoclave; Ethylene polymerizations; Tubular

Despite the intensive progress in low-pressure ethylene polymerization using gas phase and solution processes high-pressure polymerization remains important for commercial application. Presently about 22 million tonnes of polyolefins is produced in autoclave and tubular high-pressure reactors comprising about 25% of their almost 84 million tonnes worldwide annual output.

Therefore, the improvement of high-pressure ethylene polymerization reactors is still a highly essential problem. Research activities in this field provide the enhancement of economic performances for such processes and maintaining their competitiveness relating to other ethylene polymerization techniques.

This article presents a consideration of the prospects to the functional enhancement of high-pressure autoclave and tubular reactors without the development of new reactor constructions and without any modifications in the entire equipment arrangement. The performed studies are generally based on the analysis of the process modes and reaction mechanisms using various initiating systems including different peroxides and their mixtures as well as peroxide–oxygen mixtures.

The composition and structure of peroxide initiators are known to determine a number of their important technological performances [1–3], particularly the following parameters:

(1) kinetic features, thermal parameters as well as the overall efficiency of the initiator application;
(2) solubility in oils (hydrocarbons) providing a simple loading into the reactor;
(3) reduction of corrosive effect upon the equipment;
(4) safety of application and storage;
(5) hygienic and toxicological properties.

The above factors comprise a background for the selection of peroxides recommended for the application in high-pressure ethylene polymerization [1].

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Nevertheless, even for thus selected group of compounds an experimental study is often required to determine the process parameters and conditions affording the most efficient application of peroxides taking into account the consumption limits, production quality (amount of extractables) and requirement to obtain certain polymer brands. In particular, a possibility for using peroxide mixtures in autoclave reactors and peroxide–oxygen mixtures in tubular reactors is still not studied enough.

Generally, we considered the following factors affecting the efficiency of peroxide initiator application.

The most effective polymerization is provided in the case of almost complete peroxide exhaustion within the reaction mixture residence time in the reaction zone. A premature initiator consumption before the required time leads to shortening of the reaction zone, increased content of the radicals yielded therein and drop of their initiating efficiency. On the other hand, if the exhaustion time is longer than the residence period a considerable part of the initiator is removed from the reaction zone with the reaction medium flow without participating in the process initiation.

The aforementioned efficiency decrease for peroxides used in the low temperature polymerization zone (Laurox, Triganox 36, Triganox 141) can be accounted for the heterogeneous state of the reaction medium. In this case, the layer adjoining to the reactor walls is enriched with the yielded highly viscous polymer and the radical concentration gradient arises in the axial direction with polymeric radicals with higher molecular weights predominantly locating near the area filled with the highly viscous polymer phase.

Peroxide application at higher temperatures (Triganox 21) affords the process initiation at the interphase boundaries in the reaction medium providing more uniform distribution of the radicals, reducing the axial gradient of their concentration and subsequent growth of the initiator efficiency.

Performing the processes at further increased temperatures using such peroxides as Triganox 42, Triganox C, Triganox D and Triganox B provides a homogeneous reaction medium with almost complete disappearance of the concentration gradient and enhancement of the peroxide initiating ability. In these conditions, the initiation efficiency becomes significantly dependent upon the peroxide structure. This feature is mostly prominent for the bifunctional initiator Triganox D affording an effective production of a high molecular polymer in an extended temperature range relating to Triganox 42 and Triganox C likely due to a stepwise initiation involving the yielded polymeric radicals.

The possibilities for optimum application of peroxide initiators in autoclave and tubular commercial polymerization reactors are comparatively studied in this article. The first part relates to autoclave reactors providing single- or double-zone full mixing process mode with the productivity ranging from 16,000 to 20,000 tonnes per year.

1. Autoclave reactors

1.1. Initiator efficiency

In accordance with our previous experience [2] nine types of peroxide initiators were used in this study. The initiation activities for this series of peroxides are summarized in Table 1.

The analysis of these data indicates reduced initiator consumption for high temperature peroxides such as Tr-B relating to their low temperature counterparts like Tr-36. However, two peroxides are out of this general trend, i.e.

Tr-D featuring with a very high efficiency for the applied temperature range;

Tr-C characterizing with a relatively high consumption determined by its commercial application at temperatures above the optimum range in order to maintain the process stability.

A low activity observed for Laurox is determined by its poor solubility. Consequently, this initiator is presently only rarely used for ethylene polymerization.

The application of the most available and widely used initiator Tr-C was studied in different commercial autoclave installations producing PE with the melt flow index (MFI) 2 g/10 min.

1.2. Effect of the initiator Tr-C on the amount of “extractables” in polyethylene

The effect of the initiating system (Tr-C, Tr-A and Tr-42) upon the amount of “extractables” (residual low molecular oil and oligomer admixtures) in commercial single-zone autoclave reactor processes is illustrated in Table 2.

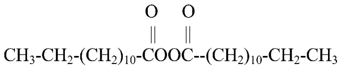
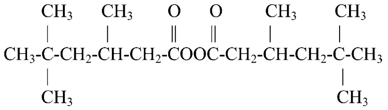
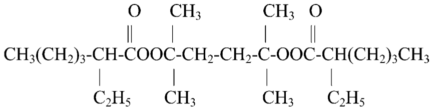
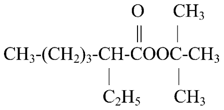
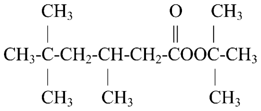
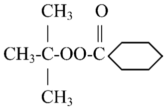
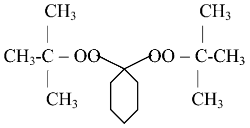
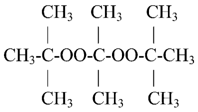
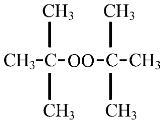
In some trials oil as a solvent for the initiators was replaced by isododecane (i-DD) in order to prevent the oil presence in the extractables. Taking into consideration the phase state of ethylene-isododecane system we assume that all i-DD from the low-pressure separator passes to the low-pressure recycle system, i.e. is not included into the polymer and extractables. For these cases, the oil fraction in the extractables comprises about 30% of its consumption.

The correlation between the specific Tr-C consumption (X) and residual content of extractables in polyethylene (A) determined as the difference between the total extractables content (E) and extractables caused by oil presence in the polymer (0.3 G) is shown in Fig. 1. The yielded extractables (low molecular polymer) amount almost linearly depend on the initiator consumption. The change of Tr-C consumption by 0.1 kg per 1 tonnes of the obtained polymer leads to a 0.1% change in the extractables content in the polymer.

If the consumption of initiator Tr-C is close to zero the extractables content falls to 0.25–0.30% with this value likely determined by other factors such as oils from compressors.

The data in the Table 2 also show that the combined effect of increased efficiency alongside with the decrease

Table 1
Effect of the structure of peroxides upon their consumption to produce 1 tonnes PE (commercial and pilot installations)

No.	Initiator brand	Formula	Consumption per 1 tonnes PE	
			kg	mol
1	Laurox	 $CH_3\text{-}CH_2\text{-}(CH_2)_{10}\text{-}\overset{O}{\overset{\parallel}{C}}OO\overset{O}{\overset{\parallel}{C}}\text{-}\text{-}(CH_2)_{10}\text{-}CH_2\text{-}CH_3$	5–6	1.8–2.5
2	Triganox 36	 $CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}\overset{O}{\overset{\parallel}{C}}OO\overset{O}{\overset{\parallel}{C}}\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_3$	2.5	1.8
3[a]	Triganox 141[a]	 $CH_3(CH_2)_3\text{-}\underset{C_2H_5}{CH}\text{-}\overset{O}{\overset{\parallel}{C}}OO\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_2\text{-}CH_2\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}OO\overset{O}{\overset{\parallel}{C}}\text{-}\underset{C_2H_5}{CH}(CH_2)_3CH_3$	2.4	0.6–1.0
4	Triganox 21	 $CH_3\text{-}(CH_2)_3\text{-}\underset{C_2H_5}{CH}\text{-}\overset{O}{\overset{\parallel}{C}}OO\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_3$	0.6	0.65–1.03
5	Triganox 42	 $CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}\overset{O}{\overset{\parallel}{C}}OO\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_3$	0.4	1.7
6	Triganox C		0.35–0.5	1.8–2.5
7[a]	Triganox 22[a]		0.47	1.8
8[a]	Triganox D[a]	 $CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}OO\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}OO\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_3$	0.14–0.24	0.6–1.0
9	Triganox B	 $CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}OO\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_3$	0.10–0.15	0.65–1.03

[a] Bifunctional peroxides.

Table 2
Experimental data on extractables and initiator and solvent consumption at the production of polyethylene with MFI = 2 g/10 min.

No.	Initiating system[a]	Extractables (wt.%)	Specific consumption, kg/tonnes (PE)	
			Oil	Initiating system
1	Tr-C/Tr-C	1.0	4.5	0.49
2	Tr-C/(Tr-C + Tr-B)	0.78	4.1	0.32
3	(Tr-C + Tr-42)/(Tr-C + Tr-B)	0.8–0.9	6.3	0.17
4	Tr-C/Tr-B	0.82	3.2	0.36
5	Tr-C/Tr-B	0.86	5.8	0.26
6	Tr-C/Tr-B	0.9	6.0	0.27
7	(Tr-C + Tr-42)/Tr-B	0.9–0.7	6.2	0.165
8	(Tr-C + Tr-42)/Tr-B	0.58	5.8	0.125
9	(Tr-C + Tr-B)/(Tr-C + Tr-B)	0.7	3.7	0.24
10	(Tr-C + Tr-42)/Tr-C	0.8	5.8	0.32

[a] Loaded into the top/bottom parts of the reactor.

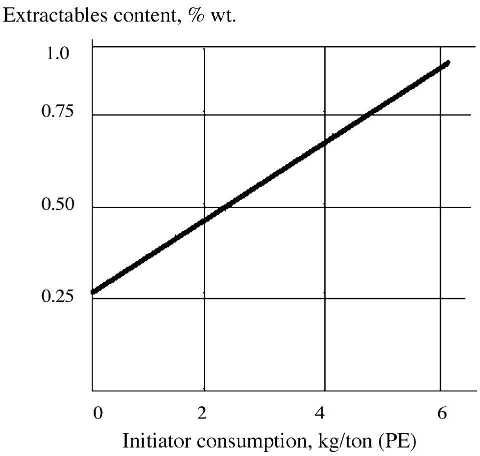


Fig. 1. Extractables content in polyethylene as function of Triganox C consumption.

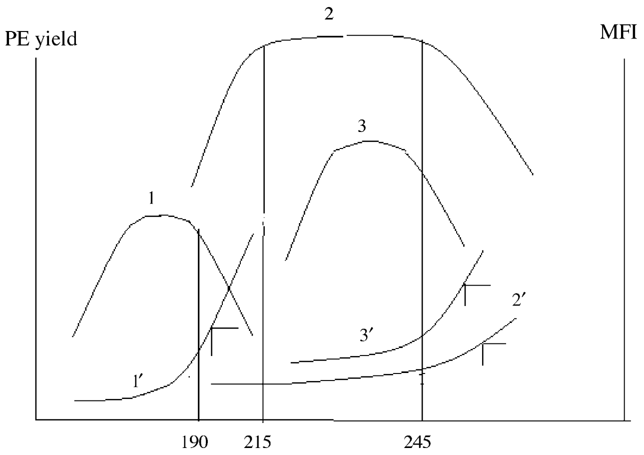


Fig. 2. Polyethylene yield and MFI as function of temperature for Triganox 36 (1 and 1′), Triganox D (2 and 2′) and Triganox C (3 and 3′).

of extractables is achieved by using initiator mixtures (Tr-C + Tr-42)/(Tr-C + Tr-B) and (Tr-C + Tr-42)/Tr-B (Trial nos. 3 and 8).

1.3. *Improvement of the process and extension of the range of polyethylene brands produced in a commercial single-zone autoclave reactor*

The processes in single-zone autoclave reactors commonly afford PE with MFI over 1 g/10 min. Polymers with MFI below this value are usually obtained in double-zone autoclave reactors with a quite low temperature in the top zone (below 200 °C) using low molecular peroxides such as Tr-36.

In order to produce PE with MFI lower than 1 g/10 min in a single-zone reactor the temperature in the top part of the reactor should be reduced by the application of a relatively low temperature peroxide in this area. However, due to a significant temperature growth along the reactor this initiator can lose its efficiency in the top part and cause a decrease of molecular weight (MFI growth) of the obtained PE.

This process is essentially shown in Fig. 2 illustrating MFI and polyethylene yield as function of temperature for three different peroxides.

The optimum process mode would be based on using each peroxide in the area of its intrinsic polyethylene yield maximum. However, monoperoxides are featured with a relatively narrow temperature range corresponding to the maximum PE yield. This complicates performing the process since in such a narrow range of optimum parameters range any occasional temperature growth or decrease in the reactor due to fluctuations of the pressure can lead to a decrease of the polymer yield, i.e. to the loss of the process thermal stability [4,5].

A decrease of the reaction medium temperature leads to the drop of the polymerization rate and heat yield causing the temperature decrease in this zone. This phenomenon promotes the further heat yield and temperature decrease and can result in the process failure.

According to the data on the polymer yield and MFI (Fig. 2) bifunctional peroxide Trigonox D is featured with a relatively wide temperature range affording polyethylene with both maximum yield and low MFI. This permits the application of this initiator in the top area of single-zone reactors with the process initiation in the temperature range from 215–218 to 240–245 °C to obtain PE with low MFI at maximum yield and consequently affords the extension of PE types produced in single-zone reactors up to MFI 0.2–0.3 g/10 min.

Generally, the performed experiments allowed us to reveal the following:

1. The application of Tr-D as a polymerization initiator provides the process stability, convenient start of the process and possibility to use the installation for obtaining polyethylenes with a broad MFI range from 0.3 to 2.0 g/10 min.
2. The replacement of the initiator Tr-C by Tr-D at the production of PE brands with MFI 2 g/10 min affords the reduction of the initiator relative weight consumption (related to the 100% initiator) by about 1.6 times at the same process parameters.
3. The replacement of the initiator mixture “Tr-C + Tr-B” by the mixture “Tr-D + Tr-B” in the top and bottom parts of the reactor affords the reduction of the relative weight consumption of Tr-D by 2.1–2.6 times compared to the consumption of Tr-C. In this case, the weight consumption of Tr-B is also decreased by 1.5 times.
4. The combined introduction of Tr-D into the top part of the reactor and Tr-D or the mixture “Tr-D + Tr-B” into the bottom part allows the decrease of ethylene pressure in the reactor from 1440–1470 to 1290 kg/cm^2 (by 150–180 kg/cm^2).
5. The use of the mixture “Tr-D + Tr-B” in the top part of the reactor in combination with “Tr-C + Tr-B” in the bottom part affords the increase of conversion providing the growth of the reactor productivity for PE with MFI 2.0 g/10 min by 15% (relative) due to the temperature decrease at the top and growth at the bottom of the reactor.

According to the comparative studies of mono and bifunctional peroxides Triganox D is found to be a promising initiator featuring with a reduced consumption during the process and providing extended temperature range of initiation and obtaining polymers with higher molecular weight relating to kinetically similar mono-peroxides. The observed effect is confirmed by experimental data for pilot and commercial installations with single-zone autoclave reactors.

2. Tubular reactors

2.1. Disadvantages of using oxygen as an initiator

Oxygen is commonly used as an initiating system in tubular reactors. This initiation method is very convenient due to the availability and low costs of oxygen and simplicity of its supply into the reaction system without additional components and special installations. However, oxygen initiation is also featured with some significant drawbacks, i.e.

1. Oxygen initiation is only possible at temperatures above 170 °C and pressures above 86 MPa.
2. The application of oxygen as a polymerization initiator almost does not allow the control over the reaction temperature. Oxygen provides only the correction of the maximum temperature level. This limitation is accounted for a significant time (7–15 min) of oxygen transportation from the feeding point to the reactor zones.
3. A significant length of the reactor zones is necessary to provide the reaction mixture heating to relatively high temperatures (190–205 °C) required for the onset of efficient initiation with oxygen. Such long zones cause a certain pressure drop, furthermore, in the course of heating the reaction mixture in the temperature range from 150 to 180 °C the initiation activity of oxygen is low leading to the formation of some amounts of a very high molecular polymer precipitating on the relatively cold internal wall of the reactor tube. This results in the decrease of the reaction mixture heating rate and usually adversely affects the polymer quality.
4. Maintaining the required temperature level of the reaction mixture in the multi-zone reactors requires the application of a sophisticated system for the control over oxygen concentrations in each of the interconnected zones. In this approach, the change of oxygen concentration in any zone requires the corresponding correction of both the total amount of oxygen supplied into the system and its redistribution over the reactor zones.
5. A certain decrease of potentially possible conversion levels and consequent reduction of technical and economic parameters of the process determined by the necessity to use relatively high “starting” temperatures for the process initiation.

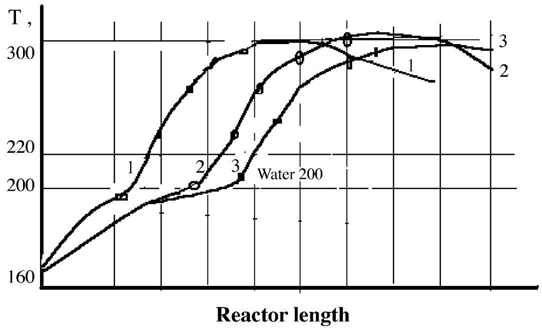


Fig. 3. Temperature profiles in the first zone of a tubular reactor with the heating water temperature 217–220 °C (1), 205 °C (2) and 195 °C (3).

2.2. Analysis of the reaction system temperature along the tubular reactor zones at oxygen initiation

Polymerization in a tubular reactor can be carried out at variation of the process parameters including such values as the temperature of heating water.

The temperature profiles for the first tubular reactor zone illustrated in Fig. 3 differ in the heating water temperature, i.e. 217–220 °C for the first (profile no. 1), 205 °C for the second (profile no. 2) and 195 °C for the third (profile no. 3) modes.

According to these data heating of the reaction mixture to the temperatures below 190 °C follows almost linear trend, i.e. the change of the reaction mixture temperature is determined by heating water. This thermal behavior suggests a very low rate of oxygen initiation at temperatures below 190–195 °C. If at these temperatures, the reaction mixture is still supplied with enough heat from the heating water (mode 1) in combination with the contribution from polymerization exothermal effect it will be sufficient for a considerable increase of the polymerization rate.

However, if the heating water temperature is close to the range indicated for the modes 2 and 3 the heat supplied from water becomes insignificant and the further heating of the reaction mixture is almost only determined by the polymerization heat. Practically, the temperature corresponding to the beginning of rapid increase in the polymerization rate can be considered as inversely proportional to the heating water temperature.

The next step of the reaction mixture temperature profile (Fig. 3) indicates that after attaining the onset temperatures an abrupt increase of the polymerization rate is observed for all of the three considered modes of the process. The reaction mixture temperature grows and the rate of its increase is almost independent on the onset temperatures.

In order to reduce the length required for heating the reaction mixture to the values below or above the oxygen initiation onset temperatures and avoid the possible negative influence of hot water at temperatures from 155–160 to 225 °C, an additional heat supply should be provided by using liquid peroxides as the process initiators.

Table 3
Specific consumption of peroxide initiators in ethylene polymerization at optimum temperatures

No.	Initiator	T_{optimum} (°C)	Specific consumption per 1 tonnes of polyethylene					
			Autoclave reactor			Tubular reactor		
			kg	mol	O_2 active	kg	mol	O_2 active
1	Triganox 36	168	2.2	7.0	35	2.8	9.0	45
2	Triganox 21	190	0.63	2.9	20			
3	Triganox 42	215	0.44	1.9	15			
4	Triganox C	230	0.39	2.0	15	0.7	3.0	20
5	Triganox B	255	0.15	1.0	10			

In contrast to oxygen, liquid peroxide initiators can be fed in any part of the reactor independently on ethylene loading with very low transportation delay period (just seconds) and controllable feeding rate. The peroxides are dissolved in different hydrocarbons with low viscosity from isododecane to oils such as “Rizella-17”.

One of the main peculiarities intrinsic to the application of peroxides as initiators is a quite narrow temperature range of effective initiation, i.e. the range of temperatures providing the minimum consumption of a certain peroxide per weight unit of the produced polymer.

The specific consumption values of various peroxide initiators at their use for ethylene polymerization in autoclave and tubular reactors in the effective temperature ranges are summarized in Table 3.

2.3. *Ethylene polymerization using combined oxygen and peroxide initiation*

The application of peroxides as initiators in combination with oxygen provides an effective approach to a series of problems relating to the improvement of ethylene polymerization in tubular reactors.

The use of low temperature peroxides in the temperature ranges corresponding to very low oxygen activity will not essentially change the temperature profile determined by oxygen initiation, just shifting this profile towards the starting point of the zone due to an intensive reaction mixture heating to the temperatures providing the onset of the efficient oxygen initiation.

Generally the application of low temperature peroxides in oxygen initiated processes affords the following advantages:

- “shifting” of the temperature profile towards the zone beginning;
- additional polymer yield at the low temperature initiation step (increase of conversion by 1% (abs.));
- “local” performance of polymerization at the low temperature step with almost no effect upon the further temperature profile of the reaction mixture.

The application of hot water with a relatively low temperature (180–185 °C) as a heating agent in combination with the mixture of peroxides such as Triganox 36 and Triganox 21 as initiators in the first tubular reactor zone provides the optimization of the tubular reactor functioning and increase of the absolute polyethylene productivity by more than 10%.

The presented considerations and experimental results show that the appropriate selection of peroxide initiators allows a significant enhancement of autoclave and tubular reactor efficiency at high-pressure ethylene polymerization.

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