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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