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COOLIGOMERIZATION OF C₉ FRACTION UNSATURATED HYDROCARBONS INITIATED BY ORGANIC PEROXIDES

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Abstract. The work deals with the cooligomerization of C₉ fraction unsaturated hydrocarbons of pyrolysis liquid products (PLP) obtained during ethylene production from diesel fuel. The main regularities of cooligomerization initiated by peroxides have been determined, the influence of the main factors (temperature, process time, initiators nature and concentration) on the yield and physico-chemical characteristics of the obtained cooligomers have been examined. The effective initiator of cooligomerization and optimal technological parameters of the process have been chosen.

Keywords: pyrolysis liquid products, hydrocarbon, peroxide, petroleum resin, cooligomerization.

1. Introduction

One of the ways of qualified usage of pyrolysis liquid by-products is cooligomerization of unsaturated products mixture present in the pyrolysis by-products. It allows to improve the performance characteristics of ethylene production and reduce the ethylene prime cost. The result of cooligomerization is obtaining of cooligomers known as petroleum resins (PR) which possess valuable operating characteristics and may be used as substituents of natural products (oil, colophony, albumine, *etc.*) in different branches of industry [1-4]. Taking into account the world tendency of increase in cost for hydrocarbon raw materials and production volume of PLP (25–30 % per raw material), its effective usage *via* deeper and wasteless processing is the key point [5-6].

Cooligomerization of C₉ fraction unsaturated hydrocarbons of PLP is one of PR production methods. Thus, in industry cumene peroxide is used for PR production. But to obtain the satisfactory yield of the target product the large process time and increased

concentration of the initiator or its dosed supply to the reaction mass are necessary. The reason is that cumene peroxide provides the effective oligomerization of styrene but at the same time it is insufficiently effective for other unsaturated hydrocarbons presented in C₉ fraction, indene first of all [7]. Therefore the search of effective initiators of the process providing the high yield of the target product and improving performance characteristics of PR production is a very urgent problem.

2. Experimental

As shown in [8-10] the reaction temperature has the essential effect on PR yield. Using thermostable initiators the higher yield of PR is achieved compared with that using the initiators with low and medium thermal stability. Therefore we investigated peroxide initiators: lauryl peroxide (LP), benzoyl peroxide (BP), *tert*-butyl peroxybenzoate (TBPB), cumene peroxide (CP), cumene hydroperoxide (CH), *tert*-butyl peroxide (TBP), *tert*-butyl hydroperoxide (TBH), *tert*-butylcumyl peroxide (TBCP), bis-(*tert*-butyl peroxyisopropyl) benzene (TPI) and “monoperoxine” (MNP) – the mixture of 1-(1-methyl-1-*tert*-butylperoxyethyl)3-isopropylbenzene and 1-(1-methyl-1-*tert*-butylperoxyethyl)-4-isopropylbenzene.

C₉ fraction (422–473 K) of diesel fuel PLP was used as a raw material for PR production. Its characteristic is given in Table 1.

Cooligomerization of C₉ fraction unsaturated hydrocarbons was carried out in temperature-controlled ampoules made from stainless steel of 100 cm³ volume in the medium of inert gas (argon) in the presence of calculated quantity of the initiator. The reaction was controlled by the change of bromine number and

cooligomerizate density. After the reaction the unreacted hydrocarbons were distilled off in two stages: first under atmospheric distillation to 463 K and then – under vacuum distillation to 473 K (residual pressure 3 GPa). The cooligomer (petroleum resin) was obtained and analyzed. The following indexes were determined: softening temperature, bromine number, color, molecular weight, dilution in a white spirit. The atmospheric and vacuum distillates were analyzed by chromatography and bromine number, color and molecular weight were determined. The cooligomerizate yield was calculated by the ratio between the weight of obtained cooligomer and initial C₉ fraction.

3. Results and Discussion

The increase in temperature (Fig. 1a), initiator concentration (Fig. 1b) and reaction time (Fig. 2) have a positive effect on the proceeding of cooligomerization of C₉ unsaturated hydrocarbons initiated by organic peroxides. This fact is confirmed by the increase in cooligomerizate density and cooligomer yield.

The positive effect of the mentioned factors (temperature, initiator concentration and process time) on the reaction proceeding is confirmed by the decrease in a bromine number, that indicates consumption of >C=C< bonds in the reaction mass with the increase in temperature (Fig. 3a), initiator concentration (Fig. 3b) and cooligomerization time (Fig. 4).

Table 1

Characteristics of the initial C₉ fraction

Indexes	Values
Density, kg/m ³	908
Bromine number, g Br ₂ /100 g	125
Molecular weight	112
Color, mg I ₂ /100 cm ³	7
Content of unsaturated compounds, wt %, including:	57.6
styrene	18.9
vinyltoluenes	8.1
dicyclopentadiene	17.8
indene	1.9

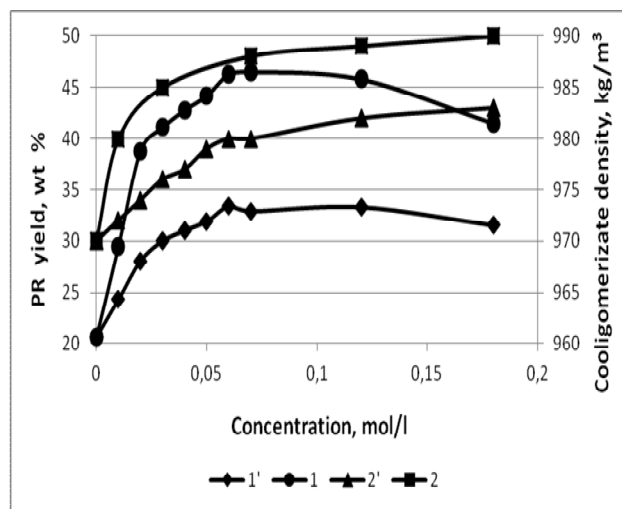
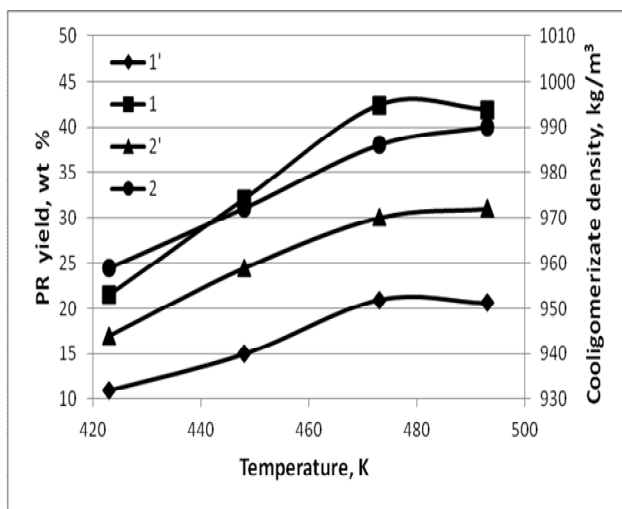


Fig. 1. Dependence of PR yield (*curves 1 and 1'*) and cooligomerizate density (*curves 2 and 2'*) on the reaction temperature (a) and initiator concentration (b). For (a): $t = 7$ h; initiator TBP in the amount of 0.04 mol/l (1 and 2); without initiator (1' and 2'). For (b): $T = 473$ K; $t = 7$ h; initiator TBP (1 and 2); initiator CH (1' and 2')

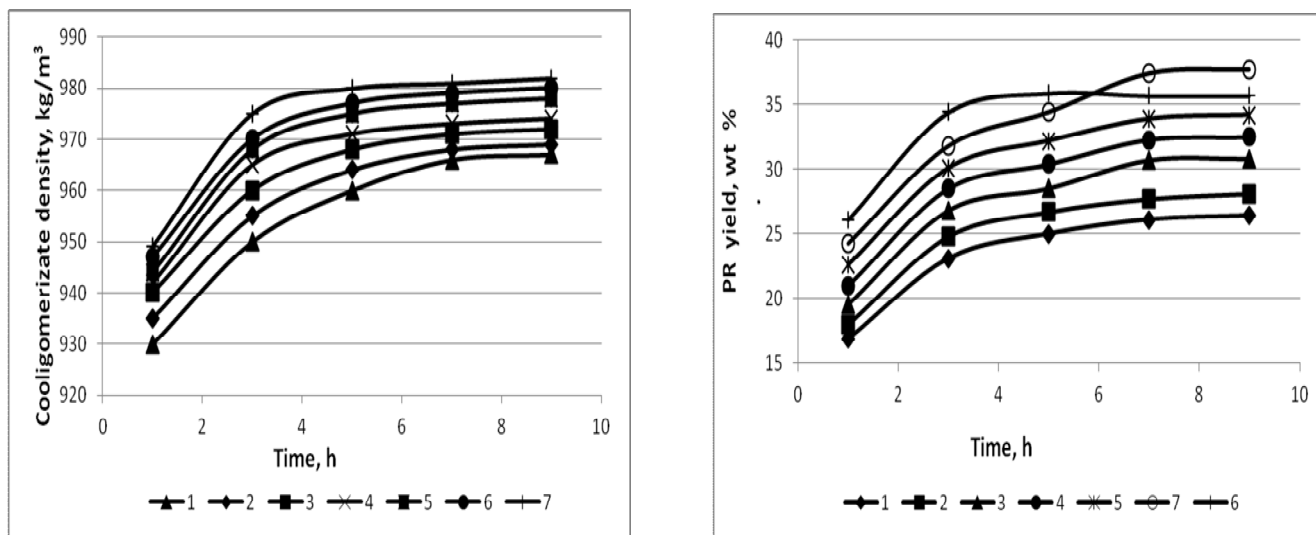


Fig. 2. Dependence of cooligomerizate density (a) and PR yield (b) on the reaction time at the temperatures (K): 423 (1); 433 (2); 443 (3); 453 (4); 463 (5); 473 (7) and 493 (6). Initiator CH in the amount of 0.06 mol/l

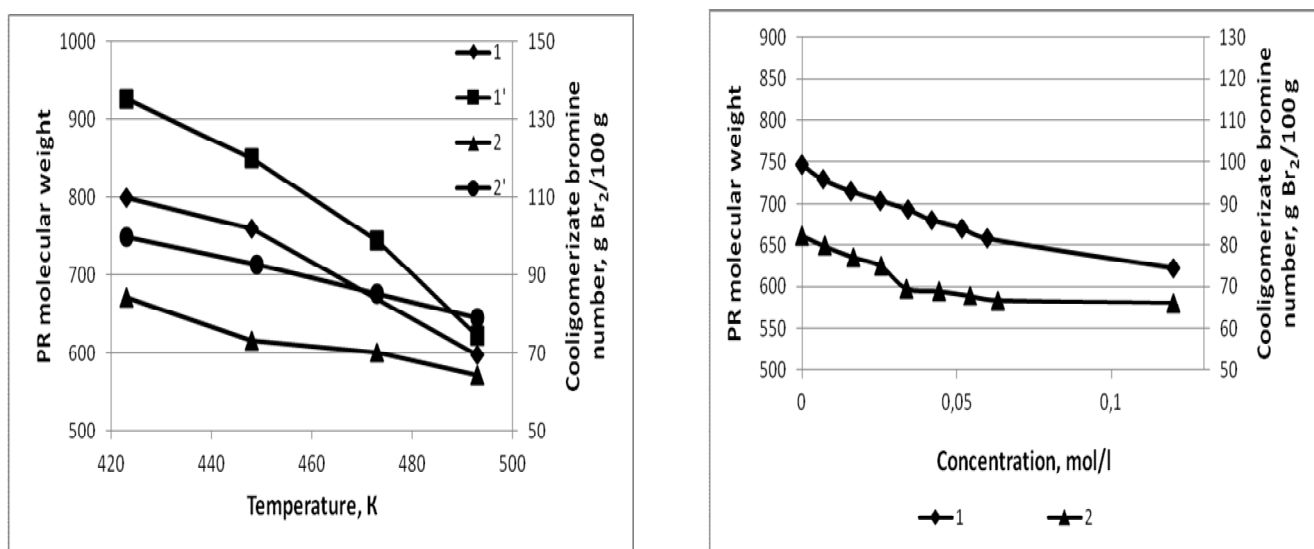


Fig. 3. Dependence of PR molecular weight (*curves 1 and 1'*) and cooligomerizate bromine number (*curves 2 and 2'*) on the reaction temperature (a) and initiator concentration (b). For (a): $t = 7$ h; initiator TBP in the amount of 0.04 mol/l (1 and 2); without initiator (1' and 2'). For (b): $T = 473$ K; $t = 7$ h; initiator TBP

The cooligomer molecular weight decreases with the increase of the reaction temperature (Fig. 3a) and initiator concentration (Fig. 3b) that is typical for radical cooligomerization. At the same time the cooligomer molecular weight is practically constant at the increase of the reaction time.

Such important value as color actually does not depend on peroxide concentration. It becomes worse with the increase in temperature and reaction time (Fig. 4). The conditions of cooligomer distillation essentially affect the

color and softening temperature of PR: with the increase in temperature and reaction time the color becomes worse and softening temperature increases. The maximally permissible temperature is within the range of 473–493 K. The further increase in temperature leads to the partial destruction of cooligomers and worsening of their color. The above-mentioned dependencies are correct for all investigated peroxides.

It should be noted that using temperature above 473 K is not reasonable because PR yield actually does

not increase but the color index becomes significantly worse. The negligible increase of density and bromine number also indicates that it is inexpedient to carry out reaction at the temperatures higher than 473 K.

The dependence of C_9 fraction unsaturated compounds conversion on the reaction temperature and time (Table 2) confirms the mentioned regularities. It was calculated according to the chromatographic analysis of C_9 fraction, atmospheric and vacuum distillates. The increase in temperature and reaction time increases the conversion of C_9 fraction unsaturated compounds. At 473 K the reaction is practically completed for 5 h. At this time the total conversion achieves 86.7 %. The increase in reaction time provides slight increase of unsaturated compounds conversion (till 88.2 % for 7 h and 90.1 % for 9 h). The temperature growth above 473 K is also accompanied by slight increase of conversion (with the increase in temperature from 473 to 498 K the conversion increases by 1.4 %). Therefore, such increase is unreasonable too.

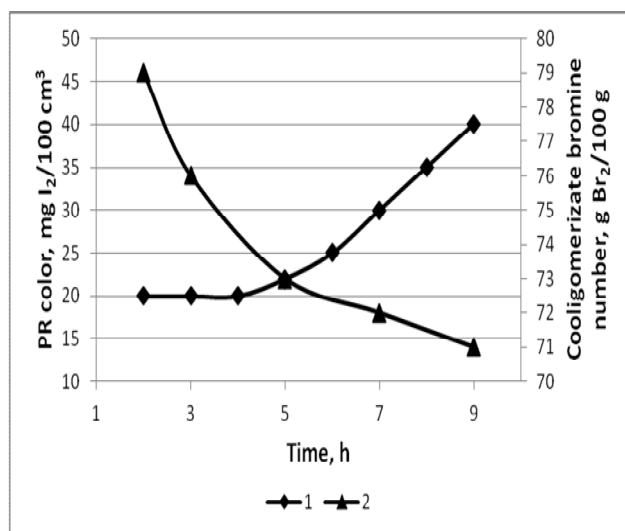


Fig. 4. Dependence of cooligomerizate bromine number (curve 2) and PR color (curve 1) on the reaction time. $T = 473$ K; initiator TBP in the amount of 0.04 mol/l

Table 2

Dependence of fraction C_9 unsaturated hydrocarbons conversion on the temperature ($t = 7$ h) and reaction time ($T = 473$ K). Initiator – TBP; $C_{in} = 0.04$ mol/l

Unsaturated hydrocarbons	Conversion (%) at the temperatures (K):				Conversion (%) at the reaction time (h)			
	423	448	473	498	1	3	5	9
Styrene	78.4	83.3	88.8	91.4	49.8	81.7	86.6	91.2
Allylbenzene	30.2	39.0	48.1	52.3	26.1	41.7	46.2	50.4
Vinyltoluenes	72.0	78.8	81.2	82.5	41.2	75.5	80.1	85.2
<i>a</i> -Methylstyrene	44.9	61.3	69.3	68.9	29.4	57.6	66.3	71.2
<i>b</i> -Methylstyrene	33.5	57.4	62.7	64.0	21.6	52.4	60.8	63.1
Indene	41.0	61.0	64.7	65.7	24.5	55.0	64.2	67.3
Methylindenes	31.2	47.6	60.2	63.6	20.2	47.4	58.2	62.2
Dicyclopentadiene	85.4	91.6	96.7	97.0	47.5	91.3	95.1	97.4
Cyclopentadiene and methylcyclopentadiene dimers	73.6	82.5	88.0	90.3	41.2	83.5	87.6	89.4
Total conversion	75.9	83.1	88.2	89.6	44.6	82.0	86.7	90.1

Table 3

Dependence of fraction C_9 unsaturated hydrocarbons conversion on initiator concentration ($T = 473$ K; $t = 7$ h; initiator TBP)

Unsaturated hydrocarbons	Conversion (%) at C_{in} (mol/l)							
	0	0.01	0.02	0.03	0.04	0.05	0.06	0.07
Styrene	70.6	70.7	79.1	83.1	88.8	89.1	89.3	89.5
Allylbenzene	29.3	44.6	47.4	47.6	48.1	48.5	48.8	49.2
Vinyltoluenes	41.3	63.3	74.6	78.3	81.2	82.6	82.9	83.1
<i>a</i> -Methylstyrene	20.5	61.3	65.4	67.6	69.3	70.5	70.8	70.9
<i>b</i> -Methylstyrene	20.1	57.1	60.4	62.3	62.7	62.9	62.8	62.8
Indene	20.0	55.9	59.3	61.0	64.7	65.1	65.6	66.0
Methylindenes	18.3	49.2	55.3	58.6	60.2	61.3	61.6	61.7
Dicyclopentadiene	54.5	85.1	96.7	96.5	96.7	96.8	96.8	96.8
Cyclopentadiene and methylcyclopentadiene dimers	51.6	70.2	82.7	86.9	88.0	88.8	89.0	89.1
Total conversion	54.8	73.0	83.2	85.7	88.2	88.7	88.9	89.0

Table 4

Dependence of PR yield on the initiator nature and concentration
(raw material – C₉ fraction, T = 473 K, t = 7 h)

Initiator	PR yield (wt %) at C _{in} (mol/l)								
	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.12	0.18
LP	19.8	23.2	23.4	27.7	29.1	30.0	30.1	30.2	30.4
BP	23.5	25.3	26.1	26.6	29.6	29.9	30.2	31.1	30.5
CH	24.4	27.0	29.9	32.3	33.4	34.0	34.1	33.1	32.3
TBH	23.6	29.4	34.0	37.5	38.6	39.3	39.0	37.4	35.3
TBPB	24.2	29.8	35.6	37.6	38.7	39.2	39.4	39.0	37.1
CP	28.0	30.1	38.2	39.4	40.4	41.3	41.4	40.6	38.1
TBCP	29.1	35.0	39.2	40.3	41.2	41.9	41.8	41.2	40.0
TBP	29.2	39.0	41.3	43.2	46.1	48.5	48.3	46.7	42.5
MNP	28.1	28.3	41.0	44.2	47.8	48.6	48.7	47.0	41.2
TPI	35.2	40.6	45.3	46.6	46.9	46.2	44.7	43.0	40.2

To establish the most effective concentration of the initiator further investigations were carried out for 7 h at 473 K and peroxide concentration of 0.01–0.18 mol/l. The increase in concentration till 0.06–0.07 mol/l favors the unsaturated compounds conversion (Table 3). It is accompanied by the increase in cooligomerizate density and PR yield (Table 4) and decrease of PR average molecular weight and bromine number.

Using the initiator with the concentration higher than 0.06 mol/l is inexpedient because in spite of the minor increase of oligomerizate density and unsaturated compounds conversion, the cooligomer yield remains almost constant. Moreover, at C_{in} > 0.12 mol/l the decrease of PR yield is observed. This fact is explained by the decrease of the molecular weight and formation of a great amount of oligomers distilled under vacuum.

While studying the effect of initiator nature on the cooligomerization process it was established that peroxides and hydroperoxides are situated in the following row (relative to PR yield): alkylperoxides > peresters > alkylhydroperoxides > acylperoxides. It means that the initiator efficiency decreases with the decrease of peroxide thermal stability. Acylperoxides (lauryl and benzoyl peroxides) are characterized by the lowest efficiency on the cooligomerization reactions caused by a high rate of their thermal decomposition under the reaction conditions. Peresters are between acylperoxides and alkylperoxides by both the rate of thermal decomposition and efficiency. The highest PR yield is provided by alkylperoxides which are characterized by low rate of their thermal decomposition at high temperatures.

Peroxides with *tert*-butyl peroxy groups provide higher PR yields compared with peroxides containing cumene peroxy groups. The higher efficiency of *tert*-butyl peroxide compared with cumene peroxide confirms the above-mentioned fact. The efficiency of *tert*-butylcumene

peroxide containing both groups takes the intermediate position. Therefore, we recommend *tert*-butyl peroxide as the initiator providing the highest PR yield at cooligomerization of C₉ fraction unsaturated compounds.

Bis-(*tert*-butyl peroxyisopropyl) benzene (TPI) containing two peroxy groups has the specific character – sequence of peroxy groups decomposition. Monoperoxide of high thermal stability is formed at the first peroxy group decomposition due to the presence of strong electron-acceptor carbonyl or hydroxyl group. Therefore, TPI is the effective initiator of the cooligomerization reaction. Even small concentrations of peroxide (0.01–0.02 mol/l) provide high (35.2–40.6 %) PR yield (Table 4). The maximum yield (45.3–46.6 %) is achieved at peroxide concentrations of 0.03–0.04 mol/l.

If we compare the efficiency of TPI and TBP, we compare the results obtained while using peroxides in the amount providing the same content of active oxygen. Under such conditions the efficiency of TPI is somewhat lower than that of TBP. While using 0.06 mol/l of TBP the cooligomerizate density and PR yield (986 kg/m³ and 45.3 %, respectively) are higher than the values obtained while using 0.03 mol/l of TPI (such concentrations provide the same content of active oxygen in the peroxides).

On the basis of statistical data manipulation we obtained the regression equations and chose optimal technological parameters for obtaining the petroleum resin. *Tert*-butyl peroxide was found to be the effective initiator of C₉ fraction unsaturated compounds cooligomerization. We recommend it for the industrial process of PR production. The optimal conditions are: TBP concentration – 0.06 mol/l (~1 wt %); cooligomerization temperature – 473 K; process time – 7 h. Under optimal conditions PR yield of 48.5 % is achieved. The product is characterized by a nice color (20 mg I₂/100 cm³) and high unsaturation (bromine number is 61.3 g Br₂/100 g).

Its softening temperature is 358 K and molecular mass – 680. The obtained resin is soluble in the white spirit and compatible with oxidized oil. We recommend to use it in lacquer-varnish industry.

4. Conclusions

We establish the regularities of cooligomerization of C₉ fraction unsaturated hydrocarbons of pyrolysis liquid products obtained during ethylene production from diesel fuel. Petroleum resins are produced. The effect of main factors (temperature, reaction time, initiator nature and concentration) on petroleum resin yield has been studied. The interrelation between the composition of peroxy initiators and their efficiency is observed. Investigated peroxides and hydroperoxides form the row according to their initiating activity (PR yield): alkylperoxides > peresters > alkylhydroperoxides > acylperoxides. While using alkyl peroxy initiator with high thermal stability the conversion of initial monomers and petroleum resins yield increase. On the basis of statistical data manipulation the regression equations were obtained and optimal parameters of petroleum resins production were chosen. The process conditions provide cooligomerization of C₉ fraction unsaturated compounds initiated by *tert*-butyl peroxide (concentration 0.06 mol/l) at 473 K for 7 h.

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ІНІЦІЙОВАНА ОРГАНІЧНИМИ ПЕРОКСИДАМИ КООЛІГОМЕРИЗАЦІЯ НЕНАСИЧЕНИХ ВУГЛЕВОДНІВ ФРАКЦІЇ C₉

Анотація. Робота присвячена дослідженню коолігомеризації ненасичених вуглеводнів фракції C₉ рідких продуктів піролізу (РПП) дизельного палива виробництва етилену. Встановлено основні закономірності ініційованої пероксидами коолігомеризації ненасичених вуглеводнів фракції C₉, з'ясовано характер впливу основних чинників (температури, тривалості реакції, природи та концентрації ініціаторів) на вихід і фізико-хімічні характеристики одержаних коолігомерів. Вибрано ефективний ініціатор коолігомеризації та оптимальні технологічні параметри процесу.

Ключові слова: рідкі продукти піролізу, вуглеводні, пероксиди, нафтополімерна смола, коолігомеризація.