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INITIATED BY ORGANIC PEROXIDES COOLIGOMERIZATION OF UNSATURATED HYDROCARBONS OF C₅ FRACTION – BY-PRODUCT OF ETHYLENE PRODUCTION

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Abstract. Initiated by organic peroxides cooligomerization of unsaturated compounds of C₅ fraction has been studied. Such fraction is a by-product obtained at ethylene production *via* hydrocarbon raw material pyrolysis. The main regularities of the process have been established, the effect of main factors (temperature, reaction time, nature and concentration of the initiators) on the yield and physico-chemical characteristics of the obtained cooligomers has been examined. The effective initiator and optimal technological parameters of the cooligomerization process have been determined

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

1. Introduction

Ethylene is one of the large-tonnage products in organic synthesis industry. It is a monomer used for production of valuable organic compounds and synthetic polymers: polyethylene, styrene, polystyrene, vinyl chloride, polyvinylchloride, butadiene, synthetic rubber, ethylene oxide and polymers on its basis, ethylene glycol, *etc.* Ethylene, the same as some other lower olefins, propylene in particular, is produced *via* pyrolysis of hydrocarbon raw material. A great amount of by-products is obtained during ethylene production. Their qualified usage is a necessity to ensure profitable and wasteless production. Taking into account the world tendency towards arising price of oil and gas, the effective use of hydrocarbon raw material *via* its deep and wasteless processing is an urgent problem.

Pyrolysis liquid products (PLP) which are formed as by-products during ethylene production in the amount

of 25–30 % (depending on pyrolysis raw material and regime) contain aliphatic and aromatic mono- and polycyclic hydrocarbons, namely benzene, toluene, xylenes, styrene, naphthalene, anthracene, *etc.* [1-2]. Usually PLP are divided into separate fractions, in which hydrocarbons with similar boiling point are concentrated.

Nowadays there is no rational scheme of PLP processing in Ukraine. The products which are produced from pyrolysis liquid by-products are: benzene, gasoline, crude for naphthalene and technical carbon production. But valuable unsaturated hydrocarbons such as styrene, isoprene, cyclopentadiene, indene and their derivatives (their amount is 15–20 wt %) are used in an unqualified way. Most of unsaturated hydrocarbons boiled till 473 K are hydrated, others – used as a raw material for technical carbon production. One of the ways of qualified application of pyrolysis liquid by-products is the cooligomerization of unsaturated hydrocarbons present in PLP and obtaining of so called petroleum resins (PR) with valuable operational characteristics which are used as the substitutes for the products of natural origin (oil, colophony, albumin, *etc.*) in different branches of industry [3-7].

One of the methods of PR production is the cooligomerization of PLP unsaturated hydrocarbons which is initiated by organic peroxides. Generally the researchers pay attention to the cooligomerization of C₉ fraction containing styrene. At the same time the publications about cooligomerization of low-boiling fraction C₅ containing valuable diene hydrocarbons (isoprene, pentadiene, cyclopentadiene, *etc.*) are limited. Therefore the investigation of cooligomerization of C₅ fraction is an urgent problem, especially the search of effective initiators and process optimal conditions.

2. Experimental

The reaction temperature has an essential effect on the PR yield [2, 8-10]. Thus, using thermostable initiators the PR yield is higher compared with the yield obtained using initiators with low and medium thermal stability. To search the effective and available initiators we studied the following peroxy initiators: *tert*-butyl hydroperoxide (TBHP), cumyl hydroperoxide (CHP), *tert*-butyl peroxide (TBP), cumyl peroxide (CP), *tert*-butylcumyl peroxide (TBCP), bis-*tert*-butylperoxyisopropyl-benzene (TBPI) and “monoperoxine” (MNP) – a mixture of 1-(1-methyl-1-*tert*-butylperoxyethyl)-3-isopropylbenzene and 1-(1-methyl-1-*tert*-butylperoxyethyl)-4-isopropylbenzene.

The fraction C₅, the characteristics of which is given in Table 1, was used as a raw material.

The cooligomerization of unsaturated hydrocarbons of C₅ fraction was carried out in temperature-controlled ampoules of 100 cm³ volume made from stainless steel in the medium of inert gas (argon) in the presence of calculated amount of the initiator. The reaction was controlled by the change of bromine number and cooligomerizate density. After the reaction the unreacted hydrocarbons were extracted *via*

cooligomerizate two-stage distillation: first at the atmospheric pressure and then at the residual pressure of 3 gPa till the temperature of 473 K. After distillation the cooligomer (petroleum resin) was obtained and was analyzed by the following characteristics: softening temperature, bromine number, color, molecular weight, solubility in white spirit. The atmospheric and vacuum distillates were analyzed using chromatography and again bromine number, color and molecular weight were determined. The cooligomerizate yield was calculated as the ratio between cooligomerizate and initial C₅ fraction weights.

3. Results and Discussion

The increase in temperature and cooligomerization time leads to the increase in cooligomerizate density and PR yield (Table 2). At the same time the bromine number decreases indicating the positive effect of the mentioned parameters on the cooligomerization process. However, high temperature has a negative effect on PR quality: color is worse, molecular weight and degree of unsaturation (bromine number) are decreased (Table 3).

Table 1

Physico-chemical parameters and hydrocarbon composition of C₅ fraction

Parameters	Parameter values
Appearance	Clear colorless liquid without foreign matters
Density, kg/m ³	752
Molecular weight	71
Bromine number, g Br ₂ /100 g	230
Color, mg I ₂ /100 cm ³	< 0.25
Refractive index, n_d^{20}	1.4580
Fraction composition, K: boiling point	303
95 % is boiled	337
Weight part of water, %	< 0.3
Hydrocarbon composition, wt %	
methylbutenes	2.4
isopentane	6.8
pentenes	6.4
pentane	2.7
pentadiene-1,4	1.9
pentadiene-1,3	7.8
isoprene	36.0
cyclopentane	2.0
cyclopentene	2.1
cyclopentadiene	17.0
cetylcyclopentadienes	2.0
benzene	6.4
non-identified	6.5

Table 2

**Effect of cooligomerization conditions on cooligomerizate characteristics and PR yield
(initiator – TBP, concentration is 0.05 mol/l)**

Temperature, K	Time, h	Pressure, MPa	Cooligomerizate density, kg/m ³	Cooligomerizate bromine number, g Br ₂ /100g	PR yield, wt%
373	1	0.6	759	198	2.1
	3		765	186	4.9
	5		772	173	8.8
	7		783	143	13.8
	9		786	140	14.5
398	1	0.8	774	177	9.5
	3		798	140	13.8
	5		809	114	17.6
	7		814	99	20.2
	9		817	94	21.8
423	1	1.2	791	144	14.3
	3		812	100	19.5
	5		829	93	23.7
	7		839	87	25.1
	9		840	84	25.3
458	1	1.6	807	121	17.1
	3		826	96	22.6
	5		835	89	24.5
	7		844	83	26.0
	9		845	81	26.3
473	1	2.0	816	99	20.5
	3		831	90	24.2
	5		840	85	25.4
	7		848	81	26.3
	9		849	80	26.5
498	1	2.4	824	96	21.8
	3		839	86	25.2
	5		846	82	26.0
	7		851	80	26.7
	9		852	79	26.9

At the same time the increase in the reaction time increases the PR molecular weight (Table 3) but decreases its bromine number and worsens the color (the same as the temperature effect).

It should be noted that at low temperatures (373–393 K) mainly liquid viscous cooligomers are obtained and only at the reaction time of 7–9 h we obtained PR with satisfactory softening temperature (353–355 K).

While analyzing the results let's note the high quality of obtained PR, in particular high bromine number and low color index, in spite of low PR yield. The maximum yield (25 wt % and higher relative to the initial fraction) is achieved at the temperature of 423 K and reaction time of 5 h. But taking into account the insignificant increase in PR yield with the temperature increase from 423 to 498 K (~3–4 wt % at the time of 5–7 h) and essential worsening of PR characteristics (color index increases twice; bromine number decreases 1.5 time; molecular weight decreases by 3–5 %) the temperature of 423 K was found to be the optimum one.

It also should be noted the essential increase in saturated vapor pressure (till 1.5 MPa and higher) at high temperatures that creates technological difficulties while process proceeding.

While analyzing the obtained results (Tables 2 and 3) the cooligomerization time of 7 h was found to be the optimum one. The increase in time has no influence on PR yield but decreases bromine number and worsens the color.

The increase in temperature and reaction time increases conversion of main resin-forming components of C₅ fraction (cyclopentadiene, isoprene and penta-1,3-diene) (Table 4).

In addition, if cyclopentadiene is active already at 373 K (conversion 89.2 % for 7 h), under the same conditions isoprene and penta-1,3-diene conversion is 21.2 and 19.1 %, respectively. Thus, the increase in temperature increases the conversion of two mentioned monomers. Taking into account a high concentration of isoprene in the raw material (37.8 wt. %) the increase in its conversion essentially influences PR yield.

Table 3

**Dependence of PR physico-chemical properties on cooligomerization conditions
(initiator – TBP, concentration is 0.05 mol/l)**

Temperature, K	Time, h	Pressure, MPa	PR softening temperature, K	PR bromine number, g Br ₂ /100 g	PR molecular weight	PR color, mg I ₂ /100 cm ³
373	1	0.6	–	147	130	3
	3		–	145	150	4
	5		–	142	165	5
	7		343	141	185	7
	9		345	140	190	7
398	1	0.8	–	136	135	5
	3		–	131	160	7
	5		344	128	170	10
	7		353	126	195	15
	9		355	125	200	20
423	1	1.2	354	122	150	7
	3		357	118	165	10
	5		358	115	175	15
	7		361	112	190	20
	9		359	110	205	30
458	1	1.6	356	109	160	10
	3		358	106	180	15
	5		358	105	190	20
	7		363	104	220	30
	9		365	102	230	30
473	1	2.0	357	100	170	15
	3		361	96	195	20
	5		364	93	220	30
	7		360	91	250	30
	9		358	90	270	40
498	1	2.4	358	92	180	30
	3		366	90	210	30
	5		363	89	260	30
	7		359	85	310	40
	9		358	83	330	60

Table 4

**Dependence of hydrocarbons conversion and PR yield on the reaction temperature
(initiator – TBP, concentration is 0.05 mol/l)**

Temperature, K	Time, h	Cyclopentadiene	Isoprene	Pentadiene-1,3	PR yield, wt %
373	1	45.0	8.2	8.0	2.1
	3	57.0	12.5	12.0	4.9
	5	87.5	19.7	18.2	8.8
	7	89.2	21.2	19.1	13.8
	1	56.5	19.0	18.1	14.3
423	3	80.2	22.4	21.5	19.5
	5	89.5	29.5	24.4	23.7
	7	95.5	35.7	25.9	25.1
	1	71.5	31.4	20.4	20.5
473	3	88.7	56.5	35.5	24.2
	5	97.8	67.8	45.0	25.4
	7	98.9	77.6	52.3	26.3

Table 5

Dependence of cooligomerizate density on initiator concentration ($T = 423\text{ K}$, $P = 1.2\text{ MPa}$; $\tau = 7\text{ h}$)

C_{in} , mol/l	CHP	TBHP	CP	TBCP	TBP	MNP	TBPI
0.01	812	814	816	815	818	806	823
0.03	820	822	825	824	829	815	833
0.05	825	827	830	830	839	824	840
0.07	830	832	834	835	841	831	845
0.09	833	835	836	838	842	835	847
0.11	836	837	837	840	843	836	848
0.13	837	838	838	842	844	837	848
0.15	838	839	838	843	844	838	848

Table 6

Dependence of PR yield on initiator concentration ($T = 423\text{ K}$, $P = 1.2\text{ MPa}$; $\tau = 7\text{ h}$)

C_{in} , mol/l	CHP	TBHP	CP	TBCP	TBP	MNP	TBPI
0.01	19.6	19.9	18.7	19.0	20.2	19.1	22.1
0.03	21.8	22.1	19.8	20.1	23.6	19.9	25.2
0.05	23.4	24.2	20.6	23.2	25.1	22.4	26.8
0.07	25.4	26.5	23.3	25.1	26.3	25.0	27.7
0.09	26.4	26.8	26.2	26.1	27.0	26.4	28.4
0.11	27.0	27.1	27.7	27.0	27.7	27.3	28.9
0.13	27.1	27.2	27.9	27.5	28.5	27.5	28.2
0.15	26.6	26.5	26.4	26.7	28.3	26.7	27.5

Table 7

Dependence of C₅ fraction hydrocarbons conversion on initiator concentration (initiator – TBP; $T = 423\text{ K}$; $\tau = 7\text{ h}$)

C_{in} , mol/l	Cyclopentadiene	Isoprene	Pentadiene-1,3
0.01	94.2	25.2	19.7
0.03	95.0	29.8	22.4
0.05	95.4	35.7	25.9
0.07	95.8	38.8	27.2
0.09	96.0	40.5	29.0
0.11	96.1	42.2	30.2
0.13	96.2	43.0	30.9
0.15	96.3	43.5	31.5

Concerning the effect of initiator nature and concentration on the cooligomerization process we observed the increase in cooligomerizate density (Table 5) and PR yield (Table 6) with the increase in initiator concentration. At the same time the molecular weight and bromine number decrease. PR color does not depend on the initiator nature and concentration.

The highest values of cooligomerizate density and PR yield are observed at initiator concentration of 0.07–0.09 mol/l. The further increase in concentration practically does not affect the PR yield and decrease in PR yield is observed at the concentration of 0.13 mol/l. The reason is a number of formed radicals providing chain break and formation of low-molecular products, hence they are stripped under vacuum distillation of cooligomerizate.

While comparing values of conversion of C₅ fraction hydrocarbons (Table 4) and PR yield it should be noted that practical PR yield is less than theoretically calculated one. This fact is explained by the possibility of proceeding other side reactions, namely monomers dimerization. A great amount of formed dimers and low-molecular liquid cooligomers are stripped under vacuum distillation resulting in the decrease of PR yield.

Concerning the effect of initiator nature on PR yield the same regularities, as for C₉ fraction cooligomerization, are observed: peroxides efficiency is decreased in the row: di-*tert*-butyl peroxide > *tert*-butylcumyl peroxide > dicumyl peroxide.

Low concentrations of monoperoxine (0.01–0.03 mol/l) are ineffective for C₅ fraction cooligomerization. At the same time its high concentrations (≥ 0.09 mol/l) provide PR yield comparable with that

obtained using the same concentrations of di-*tert*-butyl peroxide.

Using TBPI as the initiator of C₅ fraction unsaturated hydrocarbons cooligomerization allows to obtain high values of cooligomerizate density and PR yield even at low concentrations of peroxide (0.01–0.03 mol/l). But if we compare the efficiency of peroxides taking into account the active oxygen content in them, then the efficiency of TBPI relative to PR yield is lower than that of di-*tert*-butyl peroxide.

The dependence of C₅ fraction hydrocarbons conversion on the initiator concentration is represented in Table 7. The monomers conversion increases with the increase in the initiator concentration (the same as in the case of temperature increase). This particularly relates to isoprene and pentadiene-1,3, the conversions of which are low. Cyclopentadiene conversion is determined, first of all, by cooligomerization temperature.

According to the investigation results the values of diene conversion of C₅ fraction are situated in a row: cyclopentadiene>isoprene>pentadiene-1,3.

Thus, di-*tert*-butyl peroxide was found to be the most effective initiator of C₅ fraction cooligomerization. The optimum conditions of the process are: temperature 423 K; time 7 h; initiator concentration 0.07 mol/l. The obtained petroleum resin is characterized by high bromine number (112–115 g Br₂/100 g); low color index (15–20 mg I₂/100 cm³); softening temperature of 358–361 K and molecular weight of 175–190.

The obtained PR is soluble in white spirit, compatible with oxidized oil and recommended to be used for the production of paint materials.

4. Conclusions

The regularities of initiated by peroxides cooligomerization of the unsaturated hydrocarbons mixture of C₅ fraction obtained *via* diesel oil pyrolysis has been established to obtain petroleum resins. The effect of main parameters (temperature, reaction time, initiator nature and concentration) on petroleum resin yield has been studied. The interdependence of peroxide initiators structure and their efficiency for cooligomerization reaction has been determined. According to the initiated activity (value of petroleum resin yield) the investigated peroxides and hydroperoxides are situated in a row:

di-*tert*-butyl peroxide>*tert*-butylcumyl peroxide>dicumyl peroxide. Thermostable peroxide initiators provide the increase in monomers conversion and PR yield. On the basis of obtained results the optimum technological parameters have been determined for the production of petroleum resin from C₅ fraction of pyrolysis liquid by-products obtained during ethylene production: initiator – *tert*-butyl-peroxide with the concentration of 0.7 mol/l; temperature of 423 K; reaction time 7 h.

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ІНІЦІЙОВАНА ОРГАНІЧНИМИ ПЕРОКСИДАМИ КООЛІГОМЕРИЗАЦІЯ НЕНАСИЧЕНИХ ВУГЛЕВОДНІВ ФРАКЦІЇ C₅ – ПОБІЧНОГО ПРОДУКТУ ВИРОБНИЦТВА ЕТИЛЕНУ

Анотація. Робота присвячена дослідженню ініційованої органічними пероксидами коолігомеризації суміші ненасичених сполук, що містяться у фракції C₅ – побічному продукті виробництва етилену піролізом вуглеводневої сировини. Встановлено основні закономірності коолігомеризації ненасичених вуглеводнів фракції C₅. 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, пероксид, нафтополімерна смола, коолігомеризація.