UDC 667.621.6+678.74

Р. О. Субтельний, О. М. Оробчук, О. Р. Дрешер, Б. О. Дзіняк

СИНТЕЗ ЦИКЛОПЕНТАДІЄНОВОГО ОЛІГОМЕРУ НА ОСНОВІ ФРАЦІЇ С9 РІДКИХ ПРОДУКТІВ ПІРОЛІЗУ

Досліджено одержання циклопентадієнового олігомеру на основі відходів низькотемпературної дисперсійної олігомеризації вуглеводневої фракції С9. Цей спосіб дає змогу виключити стадію виділення (ди) циклопентаєнової фракції із рідких продуктів піролізу. Розглянуто ініційовану пероксидами та термічну до (ко) олігомеризацію дициклопентадієнвмісної суміші вуглеводнів. Поєднання методів низькотемпературної дисперсійної олігомеризації та до (ко) олігомеризації непрореагованих вуглеводнів дає змогу одержувати на основі вуглеводневої фракції С9 стиреновий та циклопентадієновий (ко) олігомери, що відрізняються своїми властивостями та галузями застосування.

Ключові слова: рідкі продукти піролізу, дисперсійна (ко) олігомеризація, вуглеводнева фракція С9, циклопентадієн, докоолігомеризація.

R. O. Subtelnyi, O. M. Orobchuk, O. R. Dresher, B. O. Dziniak
Lviv National Polytechnic University,
Department of Organic Products Technology

CYCLOPENTADIENE OLIGOMER SYNTHESIS BASED ON C9 FRACTION OF LIQUID PYROLYSIS PRODUCTS

The production of a cyclopentadiene oligomer based on low-temperature dispersion oligomerization of the C9 hydrocarbon fraction was studied. This method allows to exclude the stage of (di) cyclopentane fraction separation from liquid pyrolysis products. The initiation of peroxides and thermal post-(co) oligomerization of dicyclopentadiene-containing mixture of hydrocarbons were considered. The combination of methods of low temperature dispersion oligomerization and post-(co) oligomerization of unreacted hydrocarbons allows to obtain, on the basis of the C9 hydrocarbon fraction, the styrene and cyclopentadiene (co) oligomers, which differ in their properties and applications.

Key words: liquid pyrolysis products, dispersion (co) oligomerization, hydrocarbon fraction C9, cyclopentadiene, post-co-oligomerization.

Problem statement. At petroleum products pyrolysis (diesel fuel and/or gasoline) a significant amount (about 30 %) of liquid by-products of pyrolysis (LBP) is formed. Liquid by-products of pyrolysis are divided into separate fractions, for example, C_5, C_{6-8}, C_9. Based on LBP hydrocarbon fractions C_5 and C_9 respectively, are obtained aliphatic and aromatic hydrocarbon resins. Hydrocarbon resins have a wide range of applications. Particulary, hydrocarbon resins are used as film forming agents in lacquer-paint and anticorrosive coatings.

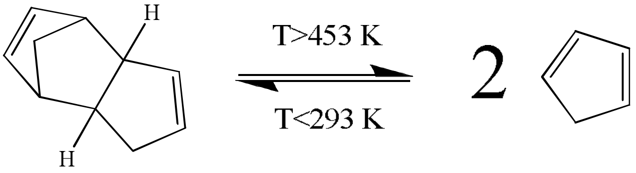
Such co-oligomers are obtained by of ionic, radical initiated and radical thermal co-oligomerization methods. Ion cooligomerization is carried out at low temperature. Its disadvantage is a high color index and an additional technological energy-consuming stage of the catalyst compartment from the reaction mixture. Cooligomerization using peroxide initiators (initiated co-oligomerization) is widely used in the industry. It allows obtaining cooligomers (hydrocarbon resins) high yield and good properties. The disadvantage of radical co-oligomerization is the high temperature of the process (453–473 K) and the complexity of the target product. The hydrocarbon resin is separated by distillation from a solution of unpolymerized fraction components.

The aromatic hydrocarbon resins obtained on the basis of the C9 fraction mainly consist of styrene-cyclopentadiene co-oligomers.

Analysis of publications. The disadvantages of the industrial method of radical co-oligomerization of the C9 fraction can be eliminated by using low-temperature dispersion co-oligomerization. Emulsion and suspension cooligomerization of hydrocarbons of fraction C9 is considered [1, 2].

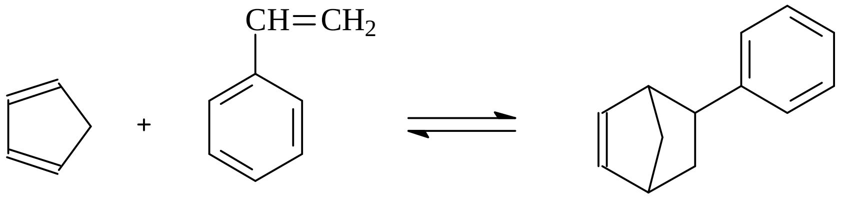
Dispersion (emulsion / suspension) co-oligomerization of unsaturated hydrocarbons of C9 fraction ensures maximum yield of the product – up to 20.0 % by weight. in terms of fraction C9. Chromatographic analysis revealed that at this stage, the styrene monomers and their derivatives are introduced into the cooligomerization reaction. In the reaction mixture remaining after the separation of the co-oligomer and distillation of the precipitant there are high-boiling reactive dicyclopentadiene, indene, residual styrene and its derivatives [1, 2].

A cycle is revealed (monomerization) of the dicyclopentadiene (DCPD) at temperatures 453–463 K with the formation of two reactive cyclopentadiene (CPD) monomers, the so-called retro-dyenic reaction Diels-Alder synthesis [3, 4]:



When heated for a long time, the DCPD can interact with the next molecule of the CPD, which joins the more atractive double bond bicyclohepene fragment. The following are sequential the joining of the CPS form a trimer, tetramer, etc., up to the formation of higher oligomers of the CPD.

It is also possible to condense a cyclopentadiene monomer with a residual styrenne according to the scheme [5]:



It was investigated the oligomerization of CPD and its dimer, DCPD to tricyclopentadiene through Diels-Alder reaction at temperatures range 393–423 K [3]. The results show that reaction temperature, pressure and solvent influence the product yield; at 423 up to 50 % yield of TCPD was obtained in the absence of solvents. The kinetics indicate that the rate is more sensitive to the concentration of CPD than to that of DCPD [3].

In the work of the authors [6] the synthesis of hydrocarbon cyclopentadiene resins on the basis of a previously allocated DCP fraction was investigated. CPD additionally allocated the fraction of the DCPD. A dedicated CPD fraction is not suitable for long-term storage.

The purpose of the work study of the basic regulatities and development of the basis of the technology of cyclopentadiene (co) oligomers on the basis of the hydrocarbon fraction C9.

Experimental results and discussion. We proposed a two-step synthesis method [7]. The first stage – dispersion (suspension / emulsion) fraction C9 hydrocarbons co-oligomerization in the temperature range

333–353 K. At this stage, a styrenic (co) oligomer is obtained. The second stage is the thermal / initiation post-cooligomerization of unreacted hydrocarbons from the first stage. The temperature of the process is 453 K. At this stage, a cyclopentadiene co-oligomer with a small number of parts of other unsaturated hydrocarbons of the C9 fraction is obtained. The scheme is shown in Figure 1

Characteristic of the initial fraction C9: density – 936 kg/m^3; bromine number – 68 g Br_2/100 g, molecular weight – 102, the content of unsaturated compounds to 45 %б including styrene – 17,85 % viniltoluene – 6,99 %, dicyclopentadiene – 18,00 %, indene – 1,25 %.

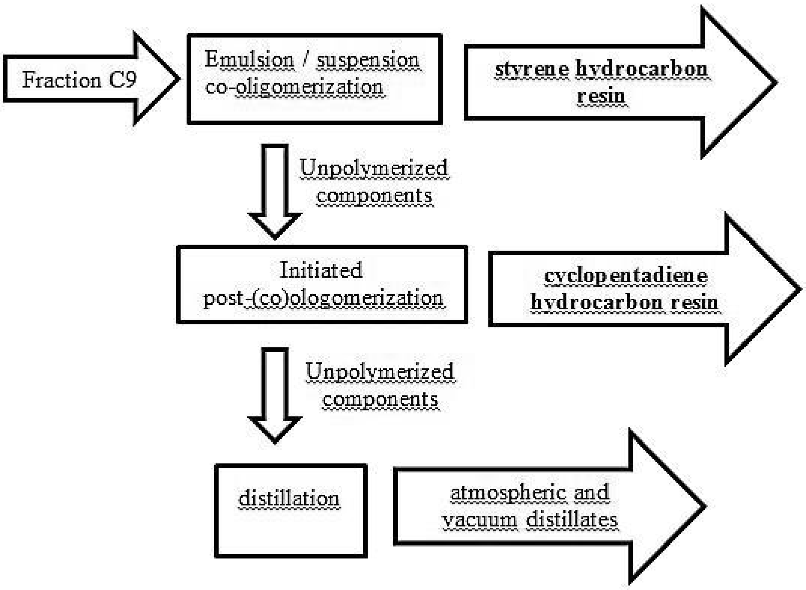


Fig. 1. Styrene and cyclopentadiene resins Scheme obtaining based on the hydrocarbon fraction C9

After the co-oligomer was isolated from the first stage of the process, the initiated post-co-oligomerization was performed in a solution of unsaturated hydrocarbons of the C9 fraction.

The process of post-co-oligomerization was carried out at a temperature of 453 K, with the addition of a suitable initiator in an amount of 1.0 % by weight. from the hydrocarbon fraction for 6 hours. The choice of temperature is due to the composition of the fraction, namely the presence of a significant amount of dicyclopentadiene (about 13.6 % by weight, calculated on the initial fraction) and its homologues.

Post-co-oligomerization was carried out in thermostatically controlled sleeves. Unreacted carbohydrates were isolated by atmospheric and vacuum distillation. For the co-oligomers obtained, color indices, unsaturation, softening temperature and molecular weight were determined. The results are shown in table. 1.

The most effective initiator according to the experimental data was Cumyl Hydroperoxide, since the total yield of the co-oligomer in two stages is 41.7 % by weight. The lower yield of the product when triggered by the reaction of coagulation of Benzoyl Peroxide occurs due to the significantly lower temperature of thermolysis, compared with di-tert-Butyl Peroxide, tert-Butyl Hydroperoxide and Cumyl Hydroperoxide. According to their physical and chemical parameters, the obtained co-oligomers are characterized by lower values of the unsaturated (bromine number) – 20,4... 23,4 g Br_2 / 100 g, higher softening temperature and molecular weight, and also significantly higher color index (80 mg I_2 / 100 ml).

The total yield of the two processes is 38,8... 41,7 % by weight. Thus, at the stage of post-co-oligomerization (in the solution of unreacted hydrocarbonson on first stage), is recommended to use Cumyl Hydroperoxide in an amount of 1,0 % by weight. (calculated on unreacted hydrocarbons of dispersion process).

Table 1

Yield and physical and chemical properties of (co) oligomers

Characteristics	Initiator			
	Benzoyl Peroxide	di-tert-Butyl Peroxide	tert-Butyl Hydroperoxide	Cumyl Hydroperoxide
Dispersion (suspension) cooligomerization ([fraction C_9]: [water] = 1:2; T = 353 K; τ = 3 hours; $C_{\text{initiator}}$ = 1,0 % wt.; $C_{stabilizer}$ = 0.1 % wt.; mixing speed – 1800 min^{-1})				
Styrene (co) oligomer yield, % by weight (calculated on the initial C_9 fraction)	19.0	13.7	9.8	16.0
Post-co-oligomerization ($C_{\text{initiator}}$ = 1.0 % wt., T = 453 K, τ = 6 hours)				
Cyclopentadiene (co) oligomer yield, % by weight (calculated on the initial C_9 fraction)	19.8	26.9	30.1	25.7
Bromine number, g Br_2/ 100 g	20.4	21.4	22.8	23.4
Softening point, K	358	358	354	350
Color by iodometric scale, mg I_2/100 ml	80	80	80	80
Molecular weight	700	725	640	670
Total yield, % by weight (calculated on the initial C_9 fraction)	38.8	40.6	39.9	41.7

As raw materials – used suspension co-oligomerisation waste (with the different initiator (Benzoyl Peroxide) dosage) [8]. The process of post-co-oligomerization was carried out at a temperature of 453 K, with a Cumyl Hydroperoxide as initiator (1.0 % wt. – calculated on the hydrocarbons fraction) duration of the process – 6 hours. The main physical and chemical parameters of co-oligomers are shown in table 2.

Table 2

Yield and physical and chemical properties of (co) oligomers

(post-co-oligomerization, $C_{\text{(Cumyl Hydroperoxide)}}$ = 1,0 % wt., T = 453 K, τ = 6 hours)

Experiment	1	2	3	4	5	6	7	8
Yield, % мас.	26.0	24.1	26.1	26.7	23.9	22.4	30.5	22.0
Bromine number, g Br_2/ 100 g	24.0	25.9	23.8	27.8	24.7	22.2	25.0	26.5
Softening point, K	355	348	352	347	357	350	354	352
Color by iodometric scale, mg I_2/100 ml	60.80	60.80	60.80	60.80	60.80	60.80	60.80	60.80
Molecular weight	650	635	640	630	640	655	655	650

Cyclopentadiene cooligomers are characterized by a lower index of unsaturation (22.2...27.8 g Br_2 / 100 g), a high softening temperature, a higher molecular weight (640–650) and a significantly higher color index – 60...80 mg I_2 / 100 ml (compared to styrene co-oligomers).

As a result of post-(co) coligomerization of unreacted residues, are obtained copolymers with a high content of cyclopentadiene units. The cyclopentadiene co-oligomer contains small amounts of styrene and vinyl-toluene units that did not react at the first stage of the process. The composition of the co-oligomers was determined based on the data of the IR-spectroscopic analysis of the samples of co-oligomers and the chromatographic analyzes of the C9 fraction and distillates.

The water and chemical stability of the CPD co-oligomer have been investigated. Characteristics of the (co) oligomer – a softening temperature of 358 K, a molecular weight of 600, a bromine number of 20,1 gBr_2 / 100 g, a color on the iodometric scale of 60...80 mg I_2 / 100 ml. The research was carried out in 10 % solutions of chloride acid, sodium hydroxide, sodium chloride and distilled water. Tests were conducted within 30 days. The results of the studies are presented in Table 3.

For comparison, in a similar conditions, the CPD oligomer was synthesized on the basis of a DCPD fraction. Characteristics of the oligomer – the softening temperature – 361 K, the molecular weight – 700, the bromine number – 18.1 g Br_2 / 100 g, the color by iodometric scale – 90 mg J_2 / 100 ml.

Table 3

Change in the mass of oligomers (30 days)

Medium	CPD (co) oligomer	CPD (co) oligomer (based on DCPD fraction)
Distilled water	0.49	0.09
Sodium chloride (10 % solution)	0.85	0.26
Sodium hydroxide (10 % solution)	0.34	0.07
Chloric acid (10 % solution)	0.11	0.24

Infrared spectroscopy of the products obtained at the post-co-oligomerization stage was carried out. Intense absorption bands of valent C-H-aromatic and CH_3-oscillations (region 2950–2916 cm^{-1}). Intense oscillations in the region of 1600–1708 cm^{-1}. These bands indicate the fluctuations of C = C bonds in polycyclic compounds, that is, confirmation of entry into the coagulum of the TPD, indene. Less intense peaks in the region 1440–1600 cm^{-1} (valence fluctuations of the aromatic nucleus) indicate the presence of benzene nuclei in the structure of the co-oligomer, as well as fragments of the peroxide initiator. The high intensity of absorption bands in the region of 1000–1175 cm^{-1} indicates the presence of 1,2-, 1,4- and 1,2,4-substituted compounds. In the region of 680–800 cm^{-1}, less intensive bands of monosubstituted aromatic compounds and intense 1,2-substituted compounds (724 cm^{-1}) are observed.

Conclusion. The possibility of synthesis of cyclopentadiene (co) oligomers on the basis of organic residues of emulsion and suspension oligomerization have been established. A comparative evaluation of the physical and chemical characteristics of cyclopentadiene resins is carried out by different methods.

1. Fuch U. Study of emulsifier nature effect on the process of hydrocarbon fraction cooligomerization in the emulsion / U. Fuch, B. Dzinyak, R. Subtelnyy // Eastern European Journal of Enterprise Technologies. – 2015. – Vol. 4(6). – P. 54–57. 2. Orobchuk O. M. Dyspersiina koolihomeryzatsiia sumishi nenasychenykh vuhlevodniv fraktsii C9: avtoref. dys. na zdobuttia stupenia kand. tekhn. nauk: spets. 05.17.04 "Tekhnolohiia produktiv orhanichnoho syntezu" / O. M. Orobchuk. – Lviv, 2015. – 2015. – 21 s. 3. Xiong Zhongqiang. Study on the oligomerization of cyclopentadiene and dicyclopentadiene to tricyclopentadiene through Diels-Alder reaction / Zhongqiang Xiong, Zhentao Mi, Xiangwen Zhang // Reaction Kinetics and Catalysis Letters. – 2005. – Vol. 85. – P. 89–97. 4. Synthesis of Cyclopentane from Dicyclopentadiene under Conditions of Concurrent Downward Flow in the Catalytic Zone of a Reactive Distillation Units / A. Baiguzing, A. Burmistrov, A. Irdinkin, P. Filina, M. // Kataliz v promyshlennosti. – 2018. – Vol. 18. – P. 6–12. 5. Copolymerization of cyclopentadiene with styrene by methylaluminoxane catalyst / Hou J., Zhang D., Lin R., Zhang D., Wang S. and Sun W.-H. // Polym. Adv. Technol. – 2006. – Vol. 17. – P. 486–490. 6. Bondaletov V. H. Yspolzovanye zhydkykh produktov pyrolyza uhlevodorodnoho syria v synteze neftepolymernykh smol / V. H. Bondaletov, L. Y. Bondaletova, Nhuen Van Tkhan // Uspekhy sovremennoho estestvoznanyia. – 2015. – No. 1(7) – S. 1130–113. 7. Dvostadiinyi sposib initsiiovanoi koolihomeryzatsii nenasychenykh vuhlevodniv fraktsii S9 / O. M. Orobchuk, R. O. Subtelnyi, Z. Iu. Maresh, B. O. Dziniak // Visnyk Natsionalnoho universytetu „Lvivska politekhnika" "Khimiia, tekhnolohiia rechovyn ta yikh zastosuvannia". – 2014. – No. 787. – S. 154–159. 8. Orobchuk O. M. Vyvchennia vplyvu dozuvannia initsiatora na protses suspenziinoi koolihomeryzatsii vuhlevodnevoi fraktsii / O. M. Orobchuk, R. O. Subtelnyi, B. O. Dziniak // Vostochno-Evropeiskyi zhurnal peredovykh tekhnolohyi "Tekhnolohyy orhanycheskykh y neorhanycheskykh veshchestv". – 2014. – No. 4/6 (70). – S. 14–18.