

*Zoriana Gnativ, Irena Nylyukyshyn, Zorian Pikh, Taras Voronchak  
and Anna Rypka*

## CATALYTIC COOLIGOMERIZATION OF STYRENE AND DICYCLOPENTADIENE: YIELD AND PROPERTIES DEPENDENCE ON REACTION MIXTURE COMPOSITION

*Lviv Polytechnic National University*

*12, S.Bandery str., 79013 Lviv, Ukraine; voronchak.taras@gmail.com*

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**Abstract.** Cationic cooligomerization of styrene and dicyclopentadiene, being main polymerizable components of C<sub>9</sub> fraction of liquid pyrolysis products of hydrocarbon feed, has been studied. Dependence of the cooligomer yield and properties including average molecular weight, softening point, bromine number, colour, and density on styrene/dicyclopentadiene ratio in the reaction mixture have been determined. Cooligomerization was carried out in solution using AlCl<sub>3</sub> based liquid catalytic complex and silica-alumina acid type catalyst that made it possible to compare the catalysts.

**Keywords:** cooligomerization, styrene, dicyclopentadiene, catalytic complex AlCl<sub>3</sub>/ethyl acetate/xylene, activated bentonite clay.

### 1. Introduction

Pyrolysis of hydrocarbons is the main process of the most important monomers – ethylene and propylene – production. Overall world pyrolysis productions capacity exceeds 160 million tons per year, including 0.5 million tons per year in Ukraine. Industrial processes of lower olefins production are inevitably accompanied by formation of about 20 % of liquid pyrolysis by-products. Efficient utilization of the by-products is an important technical and economic problem related to profitability enhancement. One of the most important direction of the liquid pyrolysis products processing is synthesis of the cooligomers known as hydrocarbon resins based on them [1, 2].

Our researches are related to the hydrocarbon resins production by cationic cooligomerization with different types of catalysts. The catalytic method of hydrocarbon resins synthesis has the following advantages: high yield, low temperature and pressure, short duration of the

cooligomerization, as well as the possibility of cooligomer properties adjustment by the process conditions change [1].

We have thoroughly investigated hydrocarbon resins synthesis from C<sub>9</sub> fraction of liquid products of diesel fuel pyrolysis when using Friedel-Crafts catalysts, namely AlCl<sub>3</sub> and liquid complexes based on it [3, 4]. We have also suggested using heterogeneous acid-type silica-alumina catalysts and studied a number of such catalysts in cooligomerization of C<sub>9</sub> fraction monomers [5-8].

The C<sub>9</sub> fraction we dealt with contains about 56 wt % of polymerizable hydrocarbons, including styrene (19 wt %), dicyclopentadiene (18 wt %), viniltoluenes (8 wt %),  $\alpha$ -methylstyrene (< 2 wt %), indene (< 2 wt %), allylbenzene (< 1 wt %), and other unsaturated substances. The main nonpolymerizable hydrocarbons include xylenes (17 wt %) and ethyltoluenes (7 wt %). However, the C<sub>9</sub> fraction composition may vary depending on the feedstock subjected to pyrolysis and the pyrolysis conditions [1, 2]. In any case, styrene (and its homologs) and dicyclopentadiene (DCPD) are the main polymerizable components. The styrene/DCPD ratio in the feedstock and consequently in the obtained cooligomer substantially determines the properties of the latter.

The study is aimed at ascertainment of the relationships between yield and properties of the cooligomer obtained by catalytic cooligomerization and styrene/DCPD ratio in the feedstock. It is also known that pure monomers, e.g. styrene, are sometimes added to the feed to adjust yield and properties of hydrocarbon resins. From this point of view this study is also useful as it allows to predict how the cooligomer yield and properties change when adding styrene or DCPD to the feedstock.

Both homogeneous and heterogeneous catalysts were used in the study. AlCl<sub>3</sub>/ethyl acetate/o-xylene catalytic complex (hereinafter just catalytic complex (CC)), having been found to be optimal among the

investigated ones [4], was used as a homogeneous catalyst. Actually, the liquid CC does not dissolve in the feed and the reaction mixture is rather fine emulsion than a solution, but we will call it “homogeneous catalysis” for convenience and as distinct from the solid silica-alumina catalyst. Heterogeneous catalytic cooligomerization was carried out with the optimal catalyst out of the investigated silica-alumina catalysts – the activated bentonite clay [5, 6]. The study, thus, allows to define how the feed composition change affects the cooligomer yield and properties when using different catalysts and makes it possible to compare these catalysts.

## 2. Experimental

### 2.1. Materials

Styrene (99 %, Aldrich) and DCPD (95 %, Merck) were used for the cooligomers synthesis. Cooligomerization was carried out in solution. So called “petrolic xylene” (*o*-, *m*- and *p*-isomers mixture with ethylbenzene admixture), that corresponds to the C<sub>9</sub> fraction composition, was used as a solvent.

For the heterogeneous catalyst preparation bentonite clay of Dashukivka deposit (Ukraine) was used. Montmorillonite content in the bentonite clay is 85 % by weight.

Liquid catalytic complex was prepared from anhydrous AlCl<sub>3</sub> (98 %, Aldrich), ethyl acetate, and *o*-xylene.

### 2.2. Catalysts Preparation

The heterogeneous oligomerization catalyst – the activated bentonite clay (ABC) was prepared as follows. Natural bentonite clay was treated with 13 wt % sulphuric acid solution taken in the amount of 60 wt % of the monohydrate of dry clay weight at 373 K for 6 h under intensive stirring. Afterwards the catalyst was filtered out, multiply washed with water until neutral pH of the scourage and dried at 423 K until constant weight.

The AlCl<sub>3</sub>/ethyl acetate/xylene liquid complex was prepared as follows. 15 g of aluminium chloride and 20.6 g of *o*-xylene were loaded into a thermally stabilized flask fitted with a stirrer and a condenser. Afterwards 5 g of ethyl acetate was dropwise added during 30 min under intensive stirring at 308 K. The reaction mixture was stirred at the same temperature for 1 h more. As a result AlCl<sub>3</sub>/ethyl acetate/*o*-xylene complex with components molar ratio equal to 1:0.5:2 was obtained.

### 2.3. Cooligomer Synthesis

In all cases the solvent content in the reaction mixture was 50 wt %. The rest 50 wt % contained styrene and/or DCPD. Cooligomerization was carried out in a

three-neck flask fitted with a stirrer and a condenser in argon atmosphere. The flask was placed into a thermostat heated to the process temperature. The instant of catalyst addition was considered to be the cooligomerization start.

Homogeneous catalytic cooligomerization with CC was carried out under the conditions found to be optimal for this catalyst in cooligomerization of C<sub>9</sub> fraction polymerizable components: temperature 353 K, duration 3 h, and the catalyst concentration 3 wt % in terms of AlCl<sub>3</sub> [3, 4].

Heterogeneous catalytic cooligomerization with ABC as a catalyst was carried out under the conditions found to be optimal for the cooligomers synthesis from C<sub>9</sub> fraction: temperature 393 K, duration 1 h, and the catalyst content in the reaction mixture 15 wt % [7, 9]. In addition, the heterogeneous catalytic cooligomerization was carried out under the optimal conditions of the homogeneous catalytic process to be able to compare these two catalysts more objectively. Before being used the catalyst was dried at 373–423 K for one hour. After the cooligomerization the catalyst was filtered out under vacuum.

The atmospheric and vacuum distillation was consequently carried out to obtain the final product in residue.

### 2.4. Cooligomer Properties Determination

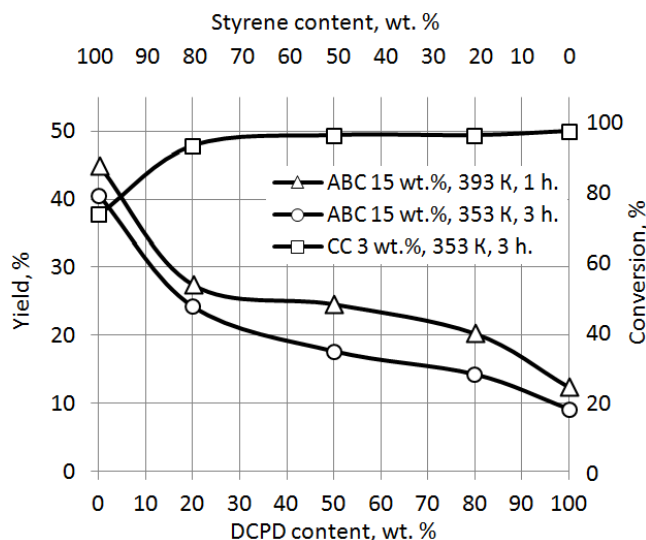
The cooligomer colour was determined by comparing its 10 wt % benzene solution with standard iodine scale. The bromine number (unsaturation) was determined by iodometric back titration according to common technique [10]. The average molecular weight was determined by cryoscopic Beckmann method in benzene solution [11]. The cooligomer density was defined by hydrostatic weighing [12].

## 3. Results and Discussion

At first, homooligomerization of styrene and DCPD was carried out. The cooligomerization itself was carried out at three styrene/DCPD ratios: 80/20, 50/50, and 20/80. Thus, we can obtain complete view of the yield and properties dependence on the initial mixture composition. In Figs. 1–3, 5, 7, and 8 weight fraction of DCPD (bottom) and styrene (top) of total amount of polymerizable components (not of the initial mixture on the whole, because 50 wt % of the mixture is the solvent) are marked on abscissa axis.

### 3.1. Cooligomer Yield

The cooligomer yield was calculated with respect to the initial mixture, *i.e.* the maximum possible yield is 50 %. The yield, calculated with respect to the polymerizable components is equal to the monomers conversion (Fig. 1).



**Fig. 1.** Cooligomer yield and monomers conversion dependence on reaction mixture composition

In case of using CC the yield is considerably higher than in case of ABC, and the monomers conversion is approximately equal to 100 %. For both catalysts the yield changes most sharply when transiting from the styrene homooligomer to styrene-DCPD cooligomer.

As can be seen from Fig. 1, there are opposite relationships for CC and ABC. In case of CC the maximum yield and almost total conversion is achieved for DCPD homooligomerization. And even small amount of DCPD dramatically raises yield in comparison with the styrene homooligomer. When using ABC as a catalyst the maximum yield is achieved on the contrary in styrene homooligomerization and DCPD content increase leads to the yield decrease.

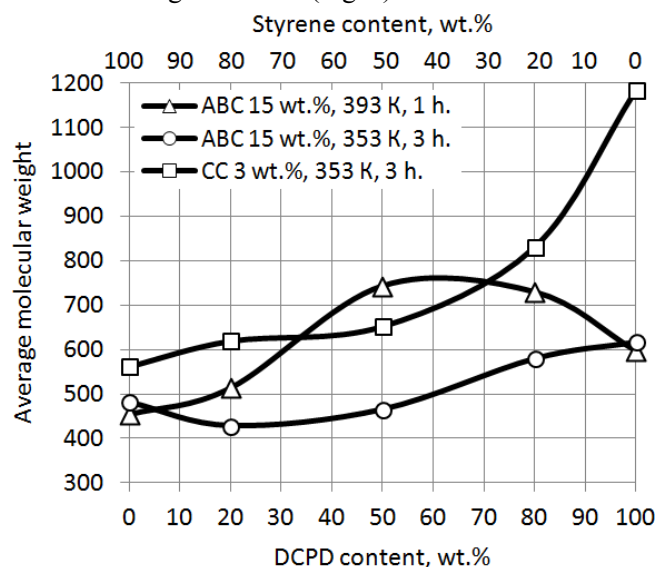
Thus, we can conclude that DCPD is more reactive than styrene when using CC. In cooligomerization with ABC as a catalyst styrene is more reactive. It is, obviously, because of DCPD molecule structure features and due to the fact that the heterogeneous catalyst active sites are fixed on its surface hindering access of DCPD. There is no accessibility problem in case of homogeneous catalysis.

The presence of two double bonds (cyclopentene and norbornene ones) in DCPD molecule makes it theoretically possible for DCPD to oligomerize by both C=C bonds (Fig. 6). However, it is possible only with homogeneous catalysts and impossible in case of using ABC as a catalyst. Since active sites are fixed on the surface, a DCPD molecule bound with the surface active site by one unsaturated bond cannot interact with other site by another double bond. It may also be the reason of higher DCPD reactivity in the cooligomerization in the presence of CC.

## 3.2. Properties of Cooligomers

### 3.2.2. Average molecular weight and softening point

In case of cooligomerization at 353 K for both catalysts the higher the DCPD content, and, respectively, the lower the styrene content, in the reaction mixture the higher the average molecular weight (Fig. 2). In case of cooligomerization with ABC at 393 K molecular weight dependence has a maximum at DCPD/styrene ratio equal to 60/40. Further increase of DCPD content leads to molecular weight decrease (Fig. 2).



**Fig. 2.** Cooligomer average molecular weight dependence on reaction mixture composition

The softening point of the cooligomer obtained by the homogeneous catalytic method is considerably higher than that of the cooligomer obtained with the heterogeneous catalyst (Fig. 3).

The softening point and the average molecular weight are closely related quantities and the regularities are often analogous for them: molecular weight increase results in softening point increase. When comparing Fig. 2 and Fig. 3, it can be seen that when raising the DCPD content softening point increases more sharply than molecular weight, and in case of ABC use at 393 K and duration of 1 h softening point increases despite the decrease of molecular weight (Fig. 3). Big difference of softening point values of the cooligomers obtained by the homogeneous and heterogeneous catalytic cooligomerization at small difference of molecular weight values indicate that there are other factors affecting the softening point value besides molecular weight.

The DCPD content increase results in softening point increase, which is especially distinct when transiting

from the cooligomer to the DCPD homooligomer. High softening point of the cooligomers obtained with CC and its dramatic increase may be explained by several reasons.

Firstly, it may be assumed that DCPD oligomerization by its both double bonds proceeds in case of high DCPD content. It results in branched and cross-linked structures formation, while, as has been already said, it is possible when using CC and hardly probable when using ABC as a catalyst.

Secondly, different ability to rotation about simple C–C bonds of the main chain may be the cause of the cooligomer with higher DCPD units content to have higher softening point.

For the oligostyrene free rotation about any C–C bond of the main chain is possible (Fig. 4a). Therefore, such cooligomer can be bended and twisted. In case of the DCPD oligomer the free rotation is possible only about the C–C bonds between the monomer units and not possible about the C–C bonds of cycloaliphatic fragments of the monomer units, i.e. about only half of the main chain bonds (Fig. 4b). Moreover, rotation about these bonds may be sterically hindered.

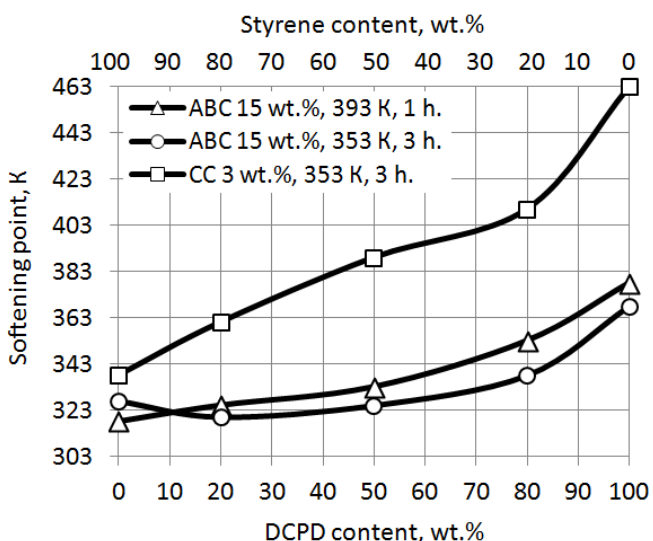


Fig. 3. Cooligomer softening point dependence on reaction mixture composition

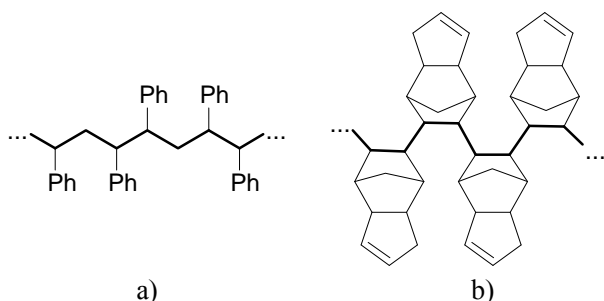


Fig. 4. Oligomer built of styrene (a) and DCPD units (when oligomerizing by norbornene bond) (b). Main chain is marked by bold line

Thus, the higher DCPD units content in the cooligomer the more rigid its main chain and, consequently, the higher the cooligomer softening point.

### 3.2.3. Bromine number

As has been already ascertained for the C<sub>9</sub> fraction, the cooligomer synthesized by the heterogeneous catalytic cooligomerization has considerably higher unsaturation compared to the product of the homogeneous catalytic cooligomerization. The results obtained for the individual monomers cooligomerization (Fig. 5), conform well to the data obtained earlier for the C<sub>9</sub> fraction [7, 9].

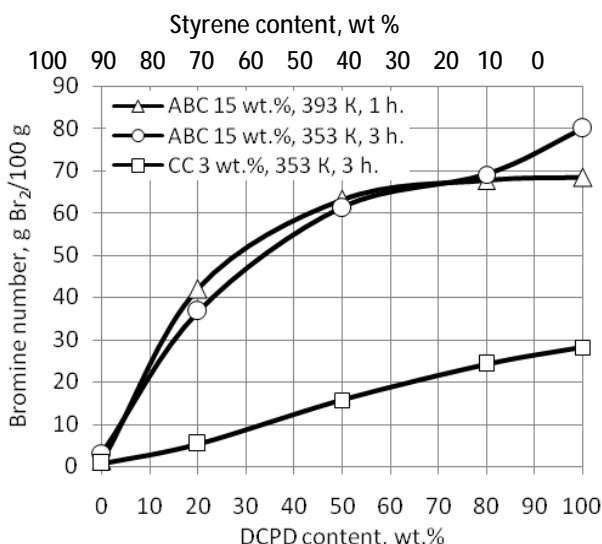
The bromine number values of the cooligomers obtained with ABC under different conditions are almost equal (Fig. 5).

The styrene homooligomer obtained with CC involves almost no double bonds. The double bonds content of the oligostyrene synthesized with ABC is very small. DCPD addition to the reaction mixture results in bromine number increase for both catalysts, but in case of the heterogeneous catalysis this increase is much more dramatic.

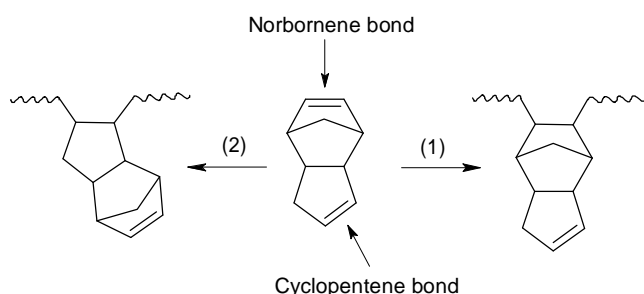
The cause of the bromine number increase when raising DCPD content is the presence of two double bonds in DCPD molecule. When cooligomerizing by one of them the other one remains in cooligomer structure causing the final product unsaturation (Fig. 6).

Another source of the cooligomers unsaturation is terminal double bonds being formed in case of chain termination by the mechanism with proton detachment from the propagating cooligomer. In case of the homogeneous catalytic cooligomerization chain termination may occur by various mechanisms. Some of them result in terminal double bond formation and some of them do not. In case of the heterogeneous catalysis chain termination occurs only by the mechanisms resulting in cooligomer with terminal double bond formation. The mechanism of chain transfer to another cooligomer molecule is not possible in this case due to the steric hindrance. The mechanisms of chain termination, in which catalyst fragment enters the cooligomer molecule, are also impossible because of the heterogeneous catalyst nature. In case of the chain termination by combination with the counterion the cooligomer molecules do not detach from the catalyst surface, and are removed from the reaction mixture along with the catalyst when the latter is filtered out.

It is for this reason, as well as, probably, due to DCPD oligomerization by both its double bonds in case of the homogeneous catalysis, that there is such a difference in unsaturation of the cooligomers obtained with CC and ABC as a catalyst.



**Fig. 5.** Cooligomer bromine number dependence on reaction mixture composition



**Fig. 6.** DCPD and corresponding monomer units being formed as a result of its oligomerization

### 3.2.3. Colour

Oligostyrene of the heterogeneous catalytic cooligomerization is pale yellow and that of the homogeneous catalytic process is brownish-orange. The colour of the styrene-DCPD cooligomers varies from reddish-orange to black depending on the monomers ratio.

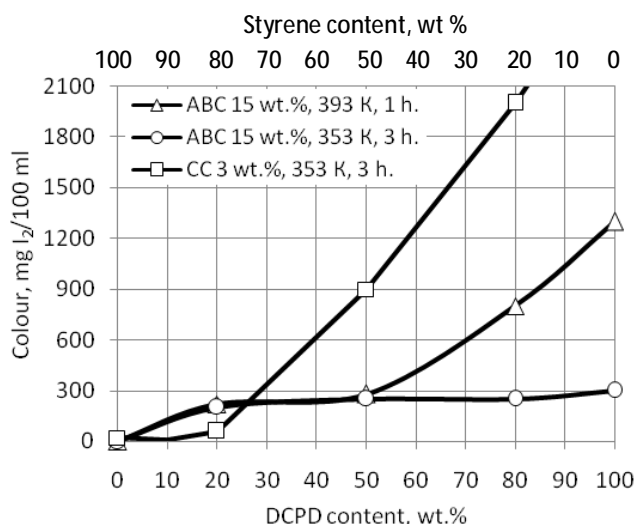
In case of the heterogeneous catalytic cooligomerization addition of only 20 wt % DCPD to the reaction mixture results in the product colour increase from 0.1 to 200 mg I<sub>2</sub>/100 ml. Further increase of DCPD content at 353 K almost does not affect the cooligomer colour, while at 393 K the colour increases further and reaches 1300 mg I<sub>2</sub>/100 ml (Fig. 7). The cooligomer colour is much darker when using CC, and oligo-DCPD colour oversteps the limits of the iodine scale at all.

### 3.2.4. Density

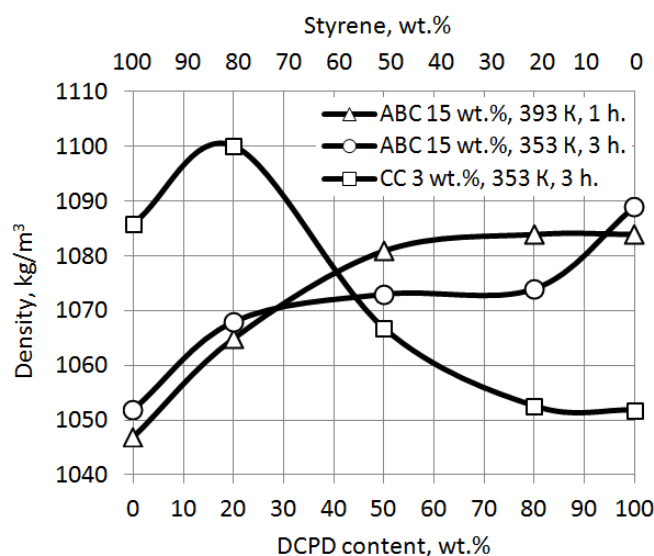
In the heterogeneous catalytic cooligomerization the raise of DCPD content in the initial mixture leads to

the cooligomer density increase (Fig. 8). The totally different regularity takes place when using CC as a catalyst. Density in this case increases only when transiting from the styrene homooligomer to the cooligomer, and further DCPD content increase results in the final product density decrease.

DCPD oligomerization by both its double bonds can be probable explanation of the cooligomer density decrease when raising DCPD content from 20 to 100 %. The branched cooligomer is obtained in case of DCPD oligomerization by both double bonds. The branched macromolecules of the cooligomer cannot be packed as densely as in case of linear polymers and the cooligomer density is less.



**Fig. 7.** Cooligomer colour dependence on reaction mixture composition



**Fig. 8.** Cooligomer density dependence on reaction mixture composition

## 4. Conclusions

The feedstock composition considerably affects both the cooligomer yield and properties, which vary in a wide range. The dependences obtained with the homogeneous and heterogeneous catalyst differ essentially. For both studied catalysts DCPD content increase results in the increase of the cooligomer bromine number, colour, and softening point. Nevertheless, character of relationships does not always coincide and there are opposite dependences for the cooligomer yield (conversion) and density.

The obtained results allow to make a hypothesis that DCPD oligomerization partially proceeds by both its double bonds when using CC as a catalyst, while in cooligomerization with ABC this is not possible. This hypothesis explains such features of the homogeneous catalytic cooligomerization as essential increase of softening point and decrease of density when increasing DCPD content, as well as considerably lower bromine number value at almost total conversion of DCPD and higher yield of the cooligomer compared to those of the process with ABC as a catalyst.

The results of the study indicate that change of styrene/DCPD ratio enable the cooligomer properties regulation in a wide range and makes it possible to achieve desirable properties of the product. Thus, to obtain cooligomer with higher softening point it is reasonable to raise DCPD content in the reaction mixture. To obtain cooligomer of light colour it is necessary to raise styrene content. If highly unsaturated cooligomer is required, it is reasonable to raise DCPD content in the reaction mixture. The given recommendations also correspond to hydrocarbon resins synthesis from the C<sub>9</sub> fraction. The hydrocarbon resins properties can be adjusted by enrichment of the fraction with styrene hydrocarbons or DCPD.

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### КАТАЛІТИЧНА КООЛІГОМЕРИЗАЦІЯ СТИРЕНУ ТА ДИЦИКЛОПЕНТАДІЕНУ: ЗАЛЕЖНІСТЬ ВИХОДУ ТА ВЛАСТИВОСТЕЙ ВІД СКЛАДУ РЕАКЦІЙНОЇ СУМІШІ

**Анотація.** Досліджено процес катіонної коолігомеризації основних смолоутворюючих компонентів фракції C<sub>9</sub> рідких продуктів піролізу вуглеводневої сировини: стирену та дициклопентадієну. Встановлено залежності виходу коолігомеру та його властивостей: середньої молекулярної маси, температури розм'якшення, ненасиченості, колірності, густини, від співвідношення стирен/дициклопентадієн у вихідній суміші. Коолігомеризацію здійснювали в розчині з використанням рідкого каталітичного комплексу на основі AlCl<sub>3</sub> та алюмосилікатного каталізатора кислотного типу, що дало можливість порівняти вищевказані каталізатори.

**Ключові слова:** коолігомеризація, стирен, дициклопентадієн, каталітичний комплекс AlCl<sub>3</sub>/етилацетат/кислота, активована бентонітова глина.