UDC 678:67.08:544.478

Production of cooligomers from C_9 fraction by two-stage thermal-catalytic method

Z.Ya. Gnativ, I.Ye. Nykulyshyn, Z.G. Pikh,
T.O. Voronchak, G.M. Rypka

National University "Lviv Polytechnic",
12, S. Bandera Str., 79013 Lviv, Ukraine, Tel.: 863-80-64

The process of cooligomers production from C9 fraction of diesel fuel pyrolysis liquid products by two-stage thermal-catalytic method was investigated. The effect of cooligomerization duration and temperature, as well as catalyst nature and concentration on the cooligomer yield and physicochemical properties has been ascertained. The optimal cooligomerization conditions have been determined. The product produced under these conditions obeys technical requirements TU U 6-05743160.020-99 for hydrocarbon resin for paint and varnish industry, and is obtained with 64,4 % yield.

1. Introduction

Nowadays pyrolysis of hydrocarbon feedstock, namely gasoline, diesel fuel and other hydrocarbon fractions is the main source of ethylene and propylene. Increase of raw materials processing depth and broadening of final products nomenclature are the main moving forces in modern petrochemical industry. From this point the synthesis of cooligomeric products – so called hydrocarbon resins (HR), by cooligomerization of unsaturated compoundsbeing components of liquid by-products of hydrocarbon feedstock pyrolysis is very urgent and perspective task. Hydrocarbon resins are produced by such world-famous companies as Exxon Mobil Corporation (USA); Eastman Chemical Company (USA); Neville Chemical Company (USA); RÜTGERS Group (Germany–Belgium); Arakawa Chemical Industries Ltd. (Japan); Puyang Zhongde Petroleum Resins Co., Ltd. (China); Shandong Qilong Chemical Co., Ltd.(China) etc. C_9 fraction of liquid products of hydrocarbon feedstock pyrolysis is used most widely as a raw material for HR production.

Cooligomers obtained from the C_9 fraction of liquid pyrolysis products are used in paint-and-varnish industry as a film-forming material and as a substituent of vegetable oils; in pulp-and-paper industry – as rosin substituent in sizing compositions and size dispersions in paper production; in rubber industry – as a plasticizer in production and reclaiming of rubber to improve elasticity and durability; in printing inks production to improve their technological properties; in protecting and corrosion resistant coatings production to improve adhesiveness of paints and mastics and to improve protecting materials hydrophobicity [1–10].

Main methods of cooligomers production from the C_9 fraction, which are industrially used by main world HR producers, are thermal (radical) cooligomerization and catalytic (cationic) cooligomerization with Friedel–Krafts catalysts ($AlCl_3$, BF_3) [2]. Both methods have some advantages and disadvantages.

Advantages of thermal method include simplicity of the process technology and light colour of HR. Disadvantages – high power inputs due to the high temperatures (473–553 K) and considerable duration (3–7 h.) of the process, relatively low HR yield, rather low molecular weight and softening point of HR and difficulty of HR properties adjustment.

Advantages of catalytic method include low temperature (< 373 K) and short duration (1–3 h.) of the process, high yield and molecular weight of HR, possibility of cooligomer properties adjustment by changing cooligomerization conditions. Complexity of technology, high cost and corrosion aggressiveness of the catalysts, as well as dark colour of HR should be mentioned as the catalytic method disadvantages.

We believe that combination of thermal and catalytic technologies should allow to combine advantages and exclude disadvantages of each method. The research, results of which are represented in present paper, was aimed on development of two-stage HR production technology, where first stage is thermal and the second one – catalytic. Such technology should enable HR production with high yield (as in case of catalytic cooligomerization) and light colour (as in case of thermal cooligomerization) at the same time. On the other hand, application of the two-stage technology should lower the final product cost due to the lowering of power input and decrease of consumption of rather expensive catalyst.

2. Experimental

2.1. Research object

The C_9 fraction of liquid pyrolysis products was our research object. Main polymerizable components are styrene, dicyclopentadiene, vinyltoluenes, α-methylsyrene, indene, allylbenzene. It should be mentioned that C_9 fraction composition may vary depending on the feedstock undergone

Table 1. **HR yield and properties dependence on catalyst type and concentration (T = 353 K, duration – 1 h; stage I: T = 532 K, duration – 3 h)**

Catalyst	$C_{cat.}$, wt. %	HR yield, %	BN, $gBr_2/100g$	M	SP, K	Colour, mg I_2/100 ml
$AlCl_3$	0,5	38,5	59,6	520	357	160
	1,0	39,2	59,7	552	375	300
$TiCl_4$	0,5	27,1	57,4	590	382	900
	1,0	49,2	59,3	547	347	900
CC	0,5	28,2	57,4	569	374	400
	1,0	40,9	56,2	515	378	500

to pyrolysis and the pyrolysis conditions.

2.2. *HR synthesis*

Anhydrous aluminium chloride, titanium chloride and $AlCl_3$/ethyl acetate/xylene catalytic complex (CC), prepared as described in [3] were used as a catalyst.

Thermal cooligomerization (stage I) was carried out in 100 ml ampoules of stainless steel placed in thermostat at temperature 523–573 K and duration 1–3 h. After the thermal stage completion the obtained cooligomerizate of stage I was cooled to the catalytic stage temperature.

The catalytic cooligomerization (stage II) was carried out in glass reactor placed in thermostat and fitted with stirrer, thermometer and reflux condenser at temperature 293–373 K and duration 0,5–2,0 h. Cooligomerizate of stage I was thermostated until the reaction temperature, afterwards required amount of catalyst was added to it.

Unpolymerized hydrocarbons were removed by consecutive atmospheric (boiler temperature – 473K) and vacuum (residual pressure – 3–4 kPa, boiler temperature – 423 K) stripping to obtain the final product – HR, in residue.

2.3. *HR characterization*

Colour of cooligomer was numerically assessed by comparison of 10 wt. % benzene solution of HR with standard iodine scale. HR unsaturation was characterized by bromine number (BN) value. It was determined by iodometric back titration according to common technique [4]. Average molecular weight (M) was determined by cryoscopy Beckmann method with benzene as a solvent. [5]. Softening point (SP) was determined by ring and ball method.

3. Results and discussion

3.1. *Study of catalyst type and concentration effect on the cooligomerization process. Determination of optimal catalyst concentration*

The thermal-catalytic cooligomerization was carried out as described above. The first stage (thermal one) was carried out at 523 K that is optimal temperature according to [1]. Temperature of the second stage (catalytic one) was 353 K that is optimal temperature according to [6]. Cooligomerization duration was 1,0 h. Since our researches of thermal-catalytic cooligomerization are aimed on reduction of energy input and specific consumption of the catalyst, the thermal stage duration was 3 h. and the catalyst concentration ($C_{cat.}$) was 0,5 and 1,0 wt. %. The obtained results are given in table 1.

Table 2. **HR yield and properties dependence on the stage II temperature: (catalyst – $AlCl_3$ ($C_{cat.}$ = 0,5 wt. %), duration – 1,0 h.; stage I: T = 532K, duration – 3 h.)**

T, K	HR yield, %	BN, $gBr_2/100g$	Colour, $mgI_2/100ml$
293	26,9	65,8	60
323	26,0	56,9	130
353	38,5	59,6	160
373	29,4	53,7	900

The highest yield of cooligomer (49,2 wt. %) is achieved when using $TiCl_4$ as a catalyst ($C_{cat.}$ = 1,0 wt. %). However, very dark colour of the cooligomer (900 mg I_2/100 ml) disables such product use in paint-and-varnish and pulp-an-paper industry. When using the catalytic complex, cooligomers are produced with lower yield (28,2–40,9 wt. %), but with better colour (400–500 mg I_2/100 ml). The best result in terms of colour (160 mg I_2/100 ml) and satisfactory yield of cooligomer (38,5 wt. %) is achieved with $AlCl_3$ as a catalyst.

The catalyst concentration increase from 0,5 to 1,0 wt. % leads to considerable increase of HR yield when using liquid catalysts ($TiCl_4$ and CC), while when using $AlCl_3$ this increase is insignificant. HR colour becomes worse when raising catalyst concentration.

Average molecular weight, softening point and BN of HR produced with the studied three catalysts are rather close. Catalyst concentration change from 0,5 to 1,0 wt. % slightly affects these properties of HR. It is clear from the obtained results that use of aluminium chloride as a catalyst with concentration 0,5 wt. % is the most favourable.

3.2. *The catalytic stage optimal temperature determination*

The next step of research was aimed on the ascertainment of the stage II temperature effect on yield and properties of the cooligomers at the same conditions of stage I (523 K, 3 h.).

The obtained results (table 2) indicate that temperature raise from 293 to 353 K leads to yield increase, while further raise of temperature has no positive effect. The yield decrease at temperatures above 353 K may be explained by considerable increase of chain termination rate at such conditions. This results in formation of some amount of low-molecular products which are distilled out during stripping.

Bromine number decreases (from 65,8 to 53,7 g Br_2/100 g) when raising temperature of the stage II. This also results in substantial increase of cooligomer colour (from 60 to 900 mg I_2/100 ml).

Molecular weight changes very slightly (fig. 1). This indicates that low-molecular compounds, formation of

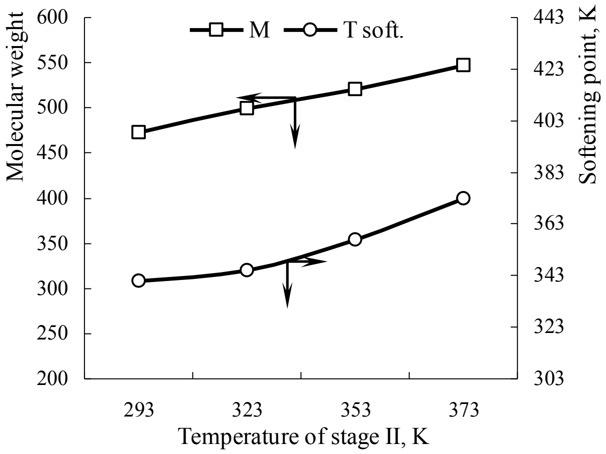

Fig. 1. HR average molecular weight and softening point dependence on the stage II temperature (catalyst – $AlCl_3$ ($C_{cat.}$ = 0,5 wt. %), duration – 1,0 h.; stage I: T = 532 K, duration – 3 h.)

which is favoured by temperature rise, are partially removed during distillation and did not enter the final product composition.

Based on the obtained results we can conclude that 353 K is an optimal temperature of the stage II, because at this temperature HR yield is maximal, its molecular weight and softening point are high and the cooligomer colour is relatively low.

3.3. The catalytic stage optimal duration determination

The effect of stage II duration on the process indicators was investigated under the same thermal stage conditions (523 K, 3 h.) and at the catalytic stage temperature found to be optimal (353K). The stage II was carried out at duration from 0,5 to 2,0 h. Duration value equal zero means that there were no catalytic stage at all (only thermal stage was carried out). The catalytic stage duration raise from 0,5 to 1,0 h. results in yield increase from 31,5 to 38,5 wt. %, while further duration raise from 1 to 2 h. leads to yield increase by 0,5 wt. % (absolute) only (fig. 2). Thus, in terms of yield, the catalytic stage duration raise over 1 h. is unreasonable.

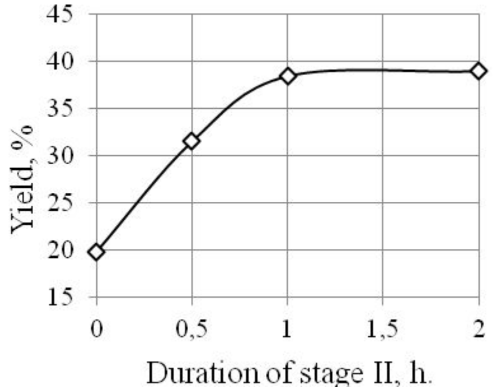

Fig. 2. HR yield dependence on the stage II duration (catalyst – $AlCl_3$ ($C_{cat.}$ = 0,5 wt. %), T = 353 K; stage I: T = 532 K, duration – 3 h.)

Table 3. **HR bromine number and colour dependence on the stage II duration (catalyst – $AlCl_3$ ($C_{cat.}$ = 0,5 wt.%), T = 353 K; stage I: T = 532 K, duration – 3 h.)**

Duration, h	BN, $gBr_2/100g$	Colour, mg I_2/ml
0	52,9	90
0,5	66,6	130
1,0	59,6	160
2,0	54,1	300

As the catalytic cooligomerization duration increases from 0,5 to 2,0 h., molecular weight and softening point naturally increase (fig. 3), because the cooligomer molecules can reach bigger size over more time. At that, duration raise from 0,5 to 1,0 h. has considerable effect, while duration raise by another hour results in very slight increase of these parameters.

Bromine number of the cooligomer obtained in the process without catalytic stage is 52,9 g Br_2/100 g, and in two-stage cooligomerization process it increases up to 66,6 (Table 3). This indicates intensive oligomerization of dicyclopentadiene (DCPD) and cyclopentadiene (CPD) formed during the thermal stage. Both substances involve two double bonds in their structure. During cationic oligomerization by one of the double bonds another one remains unreacted that causes unsaturation of the final product .As the catalytic cooligomerization increases, the product unsaturation regularly decreases.

The catalytic stage duration raise results in cooligomer colour deterioration (Table 3). That is why, in terms of HR colour, the catalytic stage duration raise over 1 h. is unreasonable.

When only thermal stage is carried out, the cooligomer yield is 19,8 wt. % only (fig. 3). However, molecular weight and softening point are higher than in the two-stage process (fig. 4). This may be explained as follows. At high temperature (523 K) and short time (1 h.) of thermal cooligomerization part of low-molecular products (dimers and

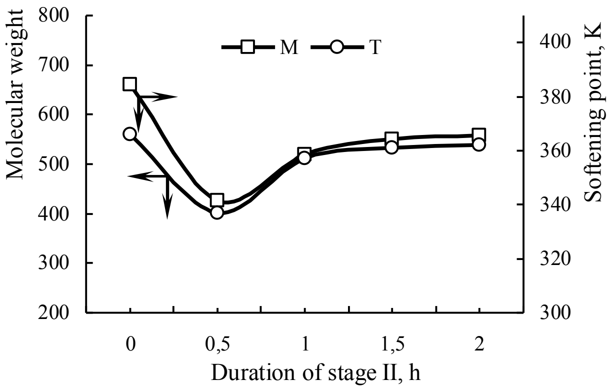

Fig. 3. HR molecular weight and softening point dependence on the stage II duration (catalyst – $AlCl_3$ ($C_{cat.}$ = 0,5 wt. %), T = 353 K; stage I: T = 532 K, duration – 3 h.)

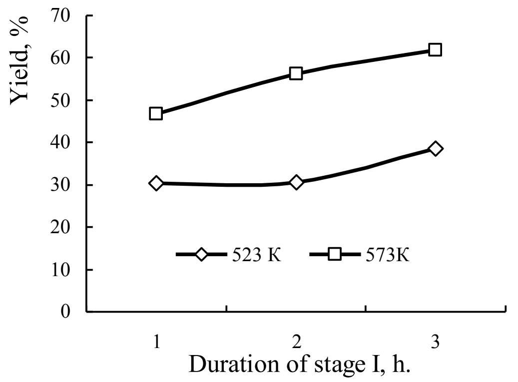

Fig. 4. HR yield dependence on temperature and duration of stage I (stage II: catalyst – $AlCl_3$ ($C_{cat.}$ = 0,5 wt. %), T = 353 K, duration – 1 h.)

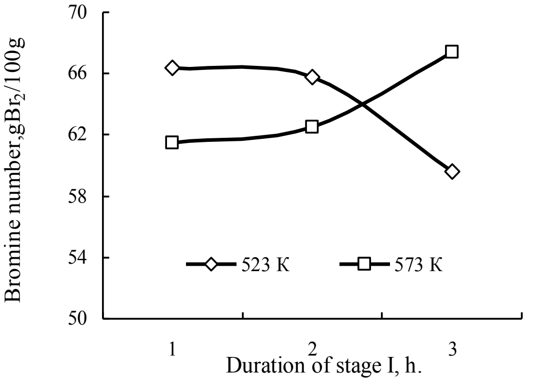

Fig. 5. HR bromine number dependence on temperature and duration of stage I (stage II: catalyst – $AlCl_3$ ($C_{cat.}$ = 0,5 wt. %), T = 353 K, duration – 1 h.)

trimers of styrene and its homologues) formed by radical mechanism is considerable. These products removed during distillation and do not enter the final product composition. The product obtained in residue contains some amount of long chains build of CPD oligomers formed by cycloaddition mechanism. Short stage of catalytic cooligomerization results in formation of great amount of medium cooligomer molecules, which enter the final product composition, resulting in lower average molecular weight of the final product. The obtained results indicate the optimal duration of the catalytic stage is 1 h.

3.4. The thermal stage optimal conditions determination

When investigating the two-stage HR synthesis process with the aim of the thermal stage optimal conditions determination, the catalytic stage was carried out under conditions found to be optimal for it: catalyst – $AlCl_3$, $C_{cat.}$ = 0,5 wt. %, T = 353 K, duration – 1 h.

Though optimal temperature of thermal stage is 523 K according to the literature [1], the process was also studied at higher temperature (573K), to find out if temperature increase has positive effect on HR yield and properties and if this allows to reduce the stage I duration.

As is clear in fig.4, the stage I temperature raise by 50 K results in considerable increase of HR yield, and this effect takes place at different process duration (1–3 h.).

BN of HR is high and varies in rather narrow range (59,6–66,4 g Br_2/100 g), as thermal stage duration changes. At 523 K BN decreases as duration increases, while at 573K BN increases on the contrary (fig. 5).

Polymerization of styrene and its homologues does not lead to unsaturated product formation. Only terminal double bonds can appear in macromolecules formed at chain termination by disproportionation in radical polymerization during the thermal stage, and at chain termination in cationic polymerization during the catalytic stage.

DCPD does not polymerize without a catalyst but at the temperatures above 443 K it monomerizes to form two molecules of CPD capable of oligomerization by Diels–Alder reaction. Such oligomerization product also does not contain double bonds in the midsection of the chain, and contains terminal double bonds only (1 or 2 per macromolecule).

DCPD monomerization results in cooligomerizate unsaturation increase, because in this reaction number of double bonds doubles. DCPD and CPD oligomerization during the catalytic stage occurs in resulting formation of the product with residual double bonds. The higher CPD content in cooligomerizate of stage I, which is further fed to the stage II, the higher the final product unsaturation is.

The higher the temperature and duration of the thermal stage are, the higher DCPD monomerization degree is. On the other hand, the shorter the first stage duration is, the greater the amount of DCPD and CPD remains unpolymerized, and during the catalytic stage the product with higher BN is formed. Ratio of DCPD monomerization rate and CPD oligomerization rate, which depends on temperature, determines the character of stage I duration effect on the final product unsaturation.

When stage I temperature is 523 K, its duration increase results in decrease of final product BN. In case of higher duration of thermal stage, greater amount of CPD, and fewer amount of DCPD and CPD remains unreacted to be able to polymerize by the scheme fig. 5 resulting in unsaturated structures formation.

At 573 K the factor of raise of the stage I oligomerizate unsaturation due to increase of monomerization degree, obviously, prevails over the factor of unsaturation decrease due to CPD.

As the stage I duration increases, molecular weight changes in the range close to its determination error. Molecular weight of the product obtained at the thermal stage temperature equal to 573 K is higher than that of HR obtained at 523 K (fig. 6). In case of one-stage thermal cooligomerization the result would be opposite, because temperature increase leads to chain termination rate increase, resulting in low molecular weight of the HR. The lower the molecular weight of the product formed in thermal cooligomerization is, the greater the number of double bonds

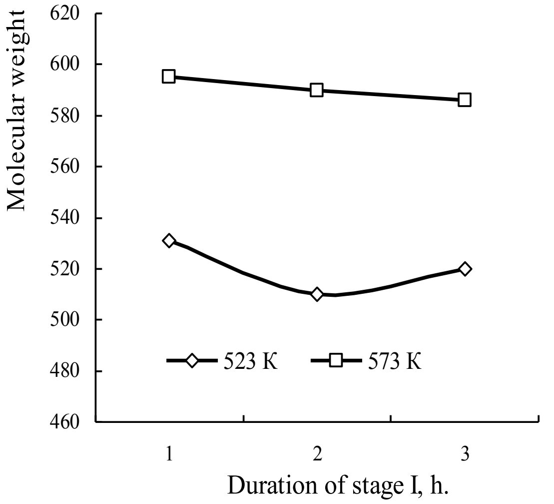

Fig. 6. HR molecular weight dependence on temperature and duration of stage I (stage II: catalyst – $AlCl_3$ ($C_{cat.}$ = 0,5 wt. %), T = 353 K, duration – 1 h.)

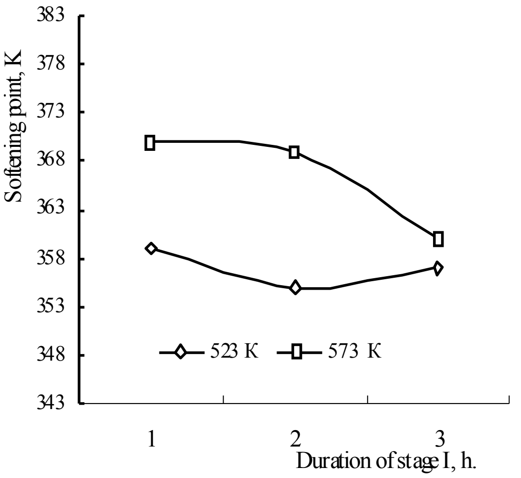

Fig. 7. HR softening point dependence on temperature and duration of stage I (stage II: catalyst – $AlCl_3$ ($C_{cat.}$ = 0,5 wt. %), T = 353 K, duration – 1 h.)

per mass unit of the cooligomerizate of stage I is. In two-stage process the low-molecular products with terminal unsaturation, formed in stage I, participate in cationic polymerization more easily due to their higher mobility. And, as is known [1], cationic polymerization allows to obtain the product with higher molecular weight. Increase of HR molecular weight, as the thermal stage decreases, also confirms the above considerations.

Softening point is higher at higher temperature of thermal stage and decreases, as its duration increases (fig. 7). This conforms well to the data obtained for molecular weight.

As stage I duration increases, HR colour decreases both at 523 K and 573 K (fig. 8). As is known, cooligomerization of styrene and its homologues results in product with light colour. The substance, which deteriorates HR colour is DCPD [3]. When DCPD (actually CPD) oligomerizes by Diels–Alder reaction (in thermal cooligomerization), the cooligomer formed is much lighter, than that produced by catalytic cooligomerization. DCPD oligomerization with Friedel–Krafts catalysts, occurring by cationic mechanism, results in products with very dark colour. It is for that, in industry, when the feedstock with high DCPD content is used, HR are usually produced by thermal method [1, 2]. If HR synthesis is carried out by catalytic method, the raw material is often previously purified from DCPD, that is rather complicated [1]. Thus, one of the ideas, underlying suggested thermal-catalytic HR production method, may be stated as follows: make as much DCPD as possible to polymerize by cycloaddition mechanism during thermal stage, for it not to deteriorate the product colour during cationic cooligomerization on the catalytic stage.

When the stage I duration increases, amount of unreacted DCPD and CPD, fed to the catalytic stage, decreases. As a result, final product colour is reduced (fig. 8). At higher temperature of thermal stage more coloured HR are obtained. This is, probably, related to the rise of amount of low-molecular cooligomers with terminal unsaturation, capable of participation in cationic cooligomerization.

Thus, in terms of colour, the optimal conditions of thermal stage are T = 523 K and duration – 3 h. Under these conditions HR colour is 130 mg I_2/100 ml. However, in terms of yield and softening point, the optimal conditions of stage I are T = 573 K and duration 2 h. The colour, however, is 400 mg I_2/100 ml.

3.5. Catalyst deactivation

All the researches described above were carried out without isolation of the catalyst from the cooligomerizate. Presence of the catalyst in cooligomerizate on distillation stage, which is carried out at temperatures up to 463 K, has negative effect on the product colour. Conventional technology of HR production from C_9 fraction by catalytic

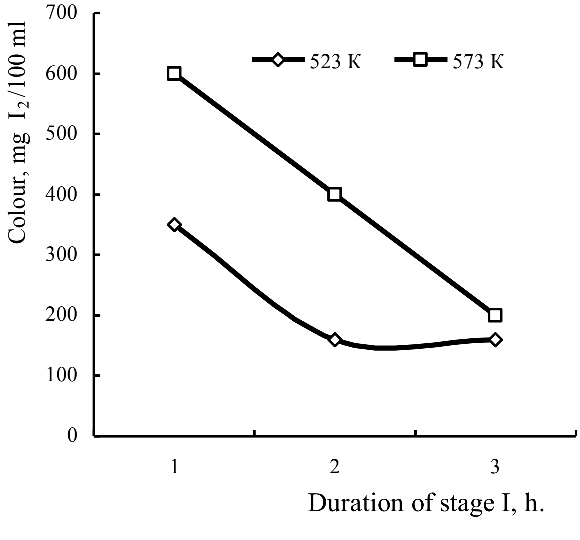

Fig. 8. HR colour dependence on temperature and duration of stage I (stage II: catalyst – $AlCl_3$ ($C_{cat.}$ = 0,5 wt. %), T = 353 K, duration – 1 h.)

Table 4. **Yield and properties of HR, synthesized from C_9fraction by thermal-catalytic method without catalyst deactivation and with deactivation of the catalyst by propylene oxide**

Stage	HR production conditions				HR yield, %	HR properties			
	Catalyst	$C_{cat.}$ %	T, K	Duration, h		BN,gBr$_2$/100g	M	SP, K	Colour, mg I$_2$/100ml
I	–	–	573	2	56,2	62,5	600	369	400
II	AlCl$_3$	0,5	353	1					
I	–	–	573	2	64,4	61,0	550	357	130
II	AlCl$_3$	0,5	353	1					
III	PO	5/1mol.	353	0,5					

method stipulates the catalyst decomposition with water, neutralization by alkali or soda solution, followed by washing and separation of the organic phase, which is than undergone stripping [7–9]. However, such method makes technology too complicated, due to the additional stages of washing, neutralization and separation, requiring additional equipment. In addition, this approach results in formation of great amount of waste water. In last years a new approach to catalyst deactivation, consisting in reaction of the latter with epoxy compounds, has been suggested [7–9]. The catalyst is, thus, deactivated, and deactivation reaction products are well compatible with HR, do not deteriorate its colour and are not to be isolated from the product. Propylene oxide (PO) was determined to be the optimal deactivating agent [7–9]. Deactivation was carried out at the second stage temperature (353 K) for 0,5 h. at molar ratio PO/AlCl$_3$ = 5/1 [4, 5].

The effect of the catalyst deactivation by propylene oxide on yield and properties of HR, produced by two-stage thermal-catalytic method under conditions, found to be optimal in terms of yield and softening point, is represented in Table 4.

As is clear from the Table 4, the catalyst deactivation allows to reduce the product colour from 400 to 130 mg I$_2$/100 ml. Bromine number remains almost constant, and molecular weight and softening point slightly decrease. In addition to considerable reduction of colour, deactivation results in increase of HR yield. The HR yield value in case of deactivation indicates, that almost all the PO enters the final product composition. When reacting with the catalyst, PO forms high-molecular compounds, that remain in HR composition after stripping. Excessive PO unreacted with the catalyst, probably, joins to the cooligomer double bonds with epoxy ring opening (O-alkylation mechanism) and, thus, enters the final product composition too.

3.6. Comparison of the two-stage thermal-catalytic method with one-stage thermal and catalytic methods

The results of two-stage cooligomerization of C_9 fraction at the optimal conditions, defined above (stage I: 573 K, 2 h.; stage II: 0,5 wt. % AlCl$_3$, 353 K, 1 h.) without deactivation (3) and with deactivation of the catalyst by propylene oxide (4); the results of one-stage thermal (1) and catalytic (6) cooligomerization at optimal conditions for each process (523 K, 6 h, for thermal one [1], and 2,5 wt. % AlCl$_3$, 373 K, 3h. for catalytic one [6]); as well as the results of one-stage thermal (2) and catalytic (5) cooligomerization

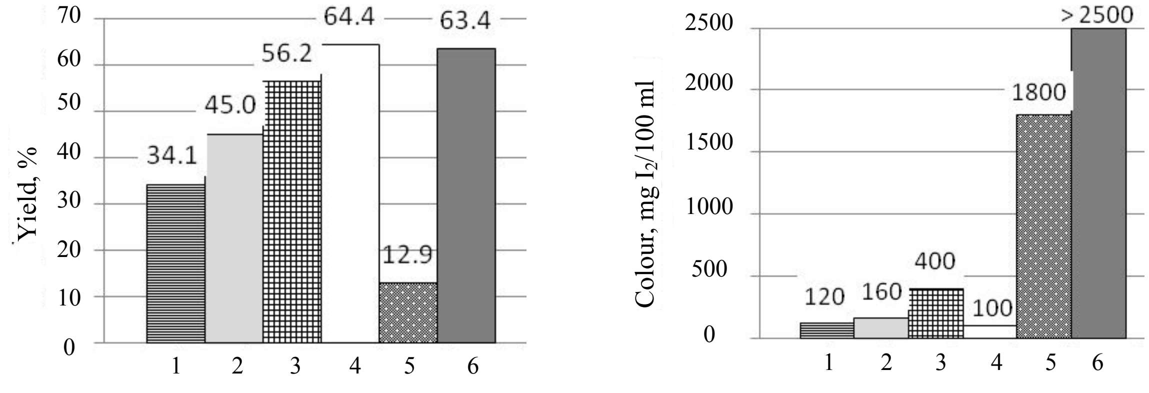

Fig. 9 – 10. HR yield and colour depending on production method

1 – thermal cooligomerization under optimal conditions: T = 523K,duration = 6 h.,

2 – thermalcooligomerization under conditions of stage I of the two-stage process: T = 573K,duration = 2 h.,

3 – two-stage cooligomerizationwithout catalyst deactivation,

4 – two-stage cooligomerization with catalyst deactivation by propylene oxide,

5 – catalytic cooligomerization under conditions of stage II of the two-stage process: AlCl$_3$($C_{cat.}$=0.5wt.%), T=353K, duration =1h.,

6 – catalytic cooligomerization under optimal conditions : AlCl$_3$ ($C_{cat.}$= 2.5 wt.%), T = 373K, duration = 3 h.

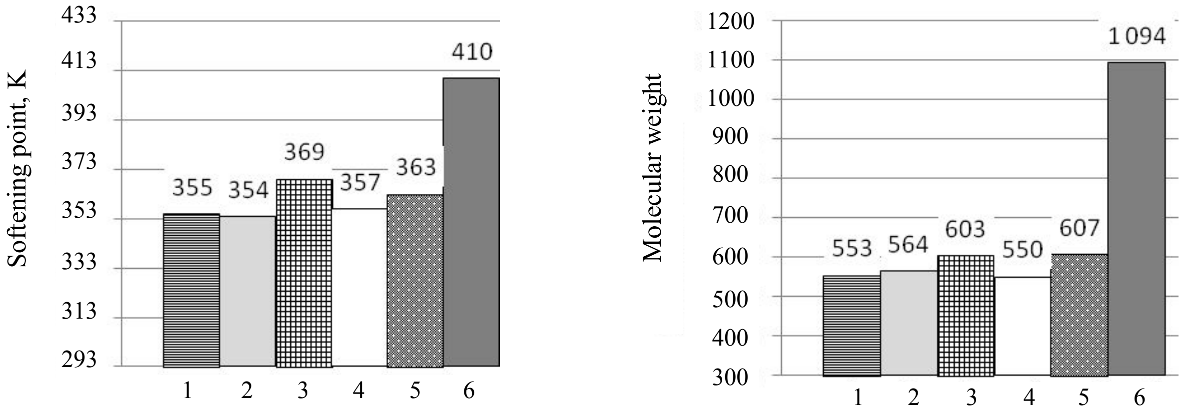

Fig. 11 – 12. HR softening point and average molecular weight depending on production method
1 – thermal cooligomerization under optimal conditions: T = 523 K, duration = 6 h.,
2 – thermal cooligomerization under conditions of stage I of the two-stage process: T = 573 K, duration – 2 h.,
3 – two-stage cooligomerizationwithout catalyst deactivation,
4 – two-stage cooligomerization with catalyst deactivation by propylene oxide,
5 – catalytic cooligomerization under conditions of stage II of the two-stage process: $AlCl_3$ ($C_{cat.}$ =0,5 wt. %), T = 353 K, duration = 1h.,
6 – catalytic cooligomerization under optimal conditions : $AlCl_3$ ($C_{cat.}$ = 2,5 wt. %), T = 373 K, duration = 3 h.

at optimal conditions of first (573 K, 2 h.) and second (0,5 wt. % $AlCl_3$, 353 K, 1 h.) stages of the two-stage process, respectively, are represented in fig. 13–17.

As is clear in fig. 9, use of two-stage technology (3) allows to increase the product yield compared to the one-stage thermal cooligomerization (1) at two times less overall duration of the process (3 h. vs. 6 h.). Catalytic stage allows to achieve total conversion of the monomers, that is impossible in thermal cooligomerization. Colour of the HR, obtained by two-stage method (fig. 14 (3)), is far better, than in case of catalytic cooligomerization (fig. 14 (6)) at almost the same yield (fig. 13). The results of catalytic cooligomerization, carried out at the second stage conditions (5), indicates that essential reduction of colour cannot be achieved just changing the catalytic process conditions (by reducing catalyst concentration and process duration) (fig. 14 (5)). Only combination of two technologies allows achieving desirable effect. In case of the catalyst deactivation by propylene oxide (4) colour of two-stage cooligomerization product is even better, than in case of thermal cooligomerization (1).

Average molecular weight and softening point of HR, obtained by the two-stage process (3–4), are almost the same, as in thermal cooligomerization (1), but lower, than in catalytic cooligomerization (fig. 11–12 (6)).

During catalytic cooligomerization DCPD reacts only by the scheme given in fig. 5 (1). High concentration (2,5 wt. %) of the catalyst in catalytic cooligomerization (6) facilitates DCPD cooligomerization by both double bonds, resulting in branched and cross-linked structures formation (fig. 13).

At low concentration of the catalyst (5) such processes are very unlikely to occur, and molecular weight and softening point of the cooligomer, that is why, are lower (fig. 11–12 (5)).

Bromine number of HR produced by different methods are rather close, but we can state, that it is higher for cooligomers produced by the two-stage method (3, 4) compared to BN of cooligomers produced by thermal method (1, 2). This is related to the differences in DCPD oligomerization mechanism in case of thermal (fig. 9) and catalytic method (fig. 5 (1)), which have been described above. In the catalytic cooligomerization more unsaturated product should be formed (fig. 5 (1)). But this is observed for the process with low catalyst concentration only (fig. 18 (5)). And in optimal conditions of the catalytic cooligomerization (6) bromine number is, on the contrary, lower. This fact confirms the supposition about DCPD cooligomerization by both double bonds (fig. 13). Bromine number of the cooligomer, obtained by the two-stage method with catalyst deactivation

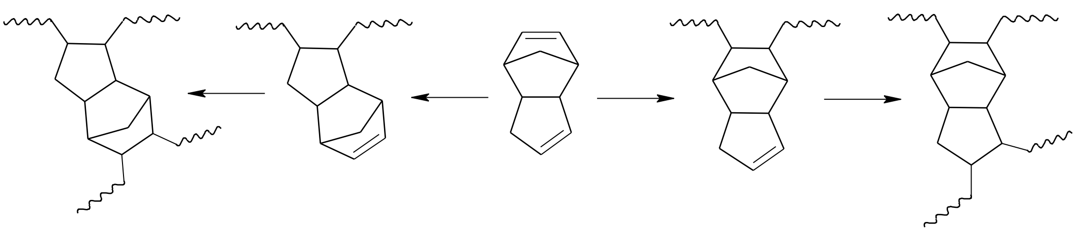

Fig. 13. Branched and cross-linked structures formation at DCPD cooligomerization by both double bonds

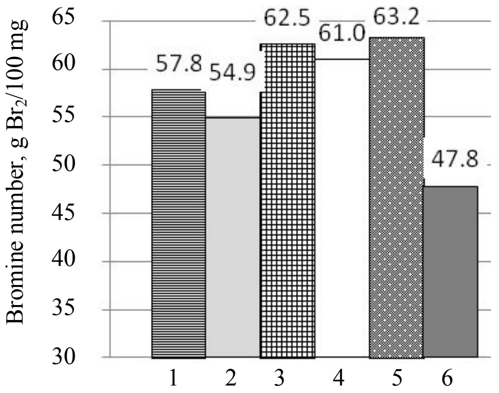

Fig. 14. HR bromine number depending on production method

(4), is lower, than in case of the process without deactivation (3). This indicates, that propylene oxide reacts not only with aluminium chloride, but with double bonds of the cooligomer as well, and enters the final product composition.

4. Conclusion

The suggested two-stage technology of HR production from C_9 fraction, where first stage is thermal and the second one is catalytic cooligomerization, allows to obtain product with high yield and good properties. This technology allows to achieve higher yield compared to the thermal method and to lower the overall process duration. Compared to the catalytic method, the two-stage technology allows to get cooligomeric product with much lighter colour at almost the same yield. It also enables to five times decrease specific catalyst consumption at the same overall process duration.

The catalyst deactivation by propylene oxide is favourable, as it results in colour improvement and yield increase.

The optimal conditions of suggested method are as follows:

Stage I: T = 573 K, duration – 2 h.; Stage II: catalyst – $AlCl_3$, $C_{cat.}$ = 0,5 wt. %, T = 353 K, duration – 1 h.; the catalyst deactivation by propylene oxide at molar ratio $AlCl_3$/PO = 1/5, T = 353 K, duration – 0,5 h.

Under these conditions HR yield is 64,4 wt. %, its colour – 100 mg I_2/100 ml, average molecular weight – 550, softening point – 357 K and bromine number – 61,0 g Br_2/100 g. These characteristics completely satisfy the requirements of the standard TU U 6-05743160.020-99 for hydrocarbon resins for paint-and-varnish industry.

1. Dumskiy Y., No B., Butov G.: *Khimia i Tekhnologiya Neftepolymernykh Smol*. Khimiya, Moscow, 1999.

2. Mildenberg R., Zander M., Collin G., *Hydrocarbon Resins*. VCH Verlagsgesellschaft mbH – A Wileycompany, Weinheim, 1997.

3. Gnativ Z., Nykulyshyn I., Pikh Z., Voronchak T., Rypka A., *Chemistry & Chemical Technology*, 2014, **2**, 165.

4. Odobashyan G. and Shvets V., *Laboratornyy Praktikum po Khimii, Tekhnologii Organicheskogo i Neftekhimicheskogo Sinteza*. Moscow, Khimiya, 1992.

5. Rudin A. and Choi P., *The Elements of Polymer Science & Engineering* (3rd Edition), Academic Press. Elsevier, New York, 2013.

6. Nykulyshyn I.Ye., *Dys.... kand. tekh. nauk*, Lviv, 1995.

7. Azanov R.Z. *Dys.... kand. khim. nauk*, Kazan, 2003.

8. Manankova A.A., Bonaletov V.H., Belousova A.C., Lapkov A.A., *Polsunovsky vestnik* (4-1), 2010, 271.

9. Fiterer H.P. *Dys....kand. khim. nauk*. Tomsk, 2006.

10. Berents A.D., Vol-Epshtein A.B., Mukhina T.M., Averkh G.L., *Processing of liquid products of pyrolysis*, Moscow, Khimiya, 1987.

Received to the editors 24.10.2014.

Получение коолигомеров из фракции C_9 двухстадийным термически-каталитическим способом

З.Я. Гнатив, И.Е. Никулишин, З.Г. Пих, Т.О. Ворончак, Г.М. Рыпка

Национальный университет “Львовская политехника”,
Украина, 79013 Львов, ул. С. Бандеры, 12, тел.: 863-80-64

Исследован процесс получения коолигомеров из фракции C_9 жидких продуктов пиролиза дизельного топлива двухстадийным термически-каталитическим способом. Установлено влияние продолжительности и температуры коолигомеризации, природы и концентрации катализатора на выход и физико-химические свойства коолигомеров. Установлены оптимальные условия коолигомеризации, позволяющие получать продукт с выходом 64,4 % масс., который соответствует ТУ У 6-05743160.020-99 на смолу нефтеполимерную для лакокрасочной промышленности.

Отримання коолігомерів із фракції C_9 двостадійним термічно-каталітичним способом

З.Я. Гнатів, І.Є. Никулишин, З.Г. Піх, Т.О. Ворончак, Г.М. Рипка

Національний університет “Львівська політехніка”,
Україна, 79013 Львів, ул. С. Бандери, 12, тел: 863-80-64

Досліджено процес отримання коолігомерів із фракції C_9 рідких продуктів піролізу дизельного палива двостадійним термічно-каталітичним способом. Встановлено вплив тривалості та температури коолігомеризації, природи та концентрації каталізатора на вихід і фізико-хімічні властивості коолігомерів. Встановлено оптимальні умови коолігомеризації, які дозволяють отримувати продукт із виходом 64,4 % мас., який відповідає ТУ У 6-05743160.020-99 на смолу нафтополімерну для лакофарбової промисловості.