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STUDYING CYCLOPENTADIENE DIMERIZATION IN HIGH-BOILING FRACTIONS OF PYROLYSIS LIQUID PRODUCTS BY MEANS OF NMR ^{1}H-SPECTROSCOPY

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Dimerisation process in composition of fractions of cyclopentadiene pyrolysis liquid products – the most reactive component has been considered. With the help of NMR ^{1}H-spectroscopy current concentrations of monomer and dimer are measured and velocity constants of demirisation are calculated.

Fractions C_5 and C_9 of liquid products of pyrolysis (LPP) contain considerable quantities of cyclopentadiene (CPD) and its dimer-dicyclopentadiene (DCPD) in its composition. CPD is extracted from fraction C_5 by means of its dimerization with further distillation. Later technical DCPD either enters to additional purification or binds with fraction C_9. At separation of liquid products of pyrolysis boiling away in temperature range from 130 to 200 °C there is a possibility to obtain fractions enriched with DCPD. Other monomers, mainly of aromatic character, enter into composition of LPP beside it [2].

It is known that DCPD is a low-active monomer at homopolymerization; however, it enters into cooligomerization reaction rather actively with aromatic monomer. At equimolar ratio of DCPD with other monomers or its excess the cooligomerization process courses with low yield of polymer, low degree of DCPD conversion. Influence of dicyclopentadiene links on technical characteristics of synthesized petroleum polymer resins (PPR) formed at polymerization of LPP fractions was studied in a number of papers [3–5]. In particular, in paper [3] it was shown that raised content of DCPD in monomer mixture results in increasing oligomer color. Besides, unreacted DCPD stays in mass (PPR) resulting in possible undesirable changes in products. DCPD removal from polymer is also technically difficult task and often results in loosing quality of obtained products.

Distillation of dicyclopentadiene fraction (DCPDF) in different conditions results in products with different ratios: CPD: DCPD. Already at low temperatures and with inhibitors CPD is dimerized into DCPD [6, 7], therefore, properties of the obtained PPR depend to a considerable degree on a choice of processing scheme of DCPDF (continuous or periodic) that is on methods of storing and accumulating fraction-raw-material. In papers [8–10] oligomerization of DCPDF was studied using catalyst systems on the basis of titanium tetrachloride and aluminum-organic compounds in the temperature range from 60 to 90 °C where it was shown that the ratio CPD : DCPD : styrene determines the choice of aluminum-organic cocatalyst and the ratio of catalyst complex components. It is obvious that identification and stabilization of original composition of LPP fractions is indispensable task at launching PPR technologies.

CPD is one of the most reactive monomers. Presence of conjugate system of double bonds and mobile hydrogen atom of α-methylene group in its molecule stipulates a tendency to reactions of condensation, addition and polymerization [11]. Owing to its very high activity CPD found wide application in laboratory and industrial practice.

Investigations in the field of CPD polymerization and copolymerization with other monomers are actual. In paper [12] formal kinetics of CPD dimerization (6,6 wt. %) in fraction C_5 and benzene in temperature range from 60 to 130 °C was studied using gas-liquid chromatography. It was shown qualitatively that CPD codimerization with pyperilene and isoprene brings insignificant error in dimerization process. However, in paper [13] more significant role of incidental processes of CPD codimerization in fraction with pyperilene and isoprene is indicated.

In paper [7] devoted to studying the influence of solvents on kinetics of CPD dimerization the values of dimerization rate constant of pure CPD at 20 °C – $20{,}2\cdot10^{-4}$ l/mole·h as well as diluted in acetonitrile, benzene, tetrachloride carbon, dichloroethane at 20 °C – $5{,}9\cdot10^{-4}$; $10{,}5\cdot10^{-4}$; $13{,}2\cdot10^{-4}$ and $17{,}6\cdot10^{-4}$ l/mole·h respectively are given.

CPD dimerization with high-boiling monomers or in composition of high-boiling fractions of LPP was not studied systematically up to date.

Experimental part

The objects of investigation are bottom products of rectifying column K-27 of the device EP-300 containing DCPD as the main monomer. Preparing fractions for studying the resinous compounds, oxidation products and different antioxidants existing in it and introduced at LPP moving along workflow lines were removed by distillation. It was stated from distillation material balance that the sum of resinous products undistillable to 200 °C, amounts to 10...12 wt. %. The composition of the given fraction and distillate were studied by the method of gas-liquid chromatography (LHM-80). Samples of fraction distilled in various conditions were stored in nitrogen atmosphere in hermetically closed ampoule in the dark at 25 °C and shaken from time to time. Spectra were measured at sample selection under nitrogen during 426 h.

Composition of DCPDF, distillate with storage stability about 24 days in nitrogen atmosphere as well as fresh distillate composition are given in Table 1.

Table 1. *Composition of dicyclopentadiene fraction of the column K-27, wt. %*

Components	Bottom products of the column K-27	Distillate of bottom products of K-27	Fresh distillate of bottom products of K-27	
			Sample 1	Sample 2
CPD	2,6	5,3	27,9	40,0
Benzene	4,5	7,3	11,6	11,5
Toluene	4,3	4,2	5,5	5,5
Ethylbenzene	0,6	0,8	1,4	1,4
P-, m-xylene	1,0	1,0	2,0	2,0
O-xylene, styrene	0,8	1,0	1,2	1,2
DCPD	63,0	62,4	27,5	15,4
Indene	15	12,9	12,0	11,9
DimethylDCPD	1,7	1,6	1,3	1,2
Unidentified hydrocarbons	6,5	3,5	9,6	9,9

At DCPDF distillation its main component – DCPD is depolymerized forming CPD. Later, at distilled fractions storing the reversible reactions of dimerization, trimerisation and so on occur, Fig. 1.

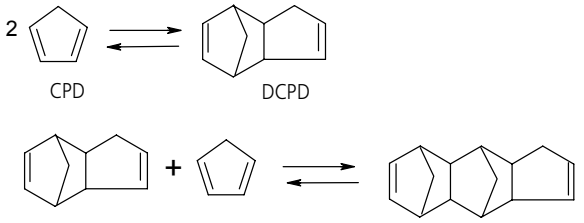

Fig. 1. *Reaction of dimerization and trimerisation of cyclopentadiene*

In the given paper the process of CPD dimerization in composition of LPP fraction with boiling-off limits 130...190 °C was considered with the help of method of NMR ^{1}H-spectroscopy. The choice of the method is connected with thermal instability of one of participants of equilibrium reaction – DCPD which starts depolymerizing already at temperatures about 100 °C. Therefore applying method of gas-liquid chromatography using column temperature to 200 °C seems to be unappropriate owing to the possible errors at analyzing. Changes in spectra NMR ^{1}H occurring at storing DCPDF samples after distillation with different ratio of CPD: DCPD concentrations were considered in the paper. Spectra were measured in $CDCl_3$ with the help of NMR spectrometer «AVANCE AV 300» («Bruker») inner standard, 20 °C. Fraction concentration in $CDCl_3$ is 20 wt. %.

Spectra NMR ^{1}H DCPD of 96 % purity and products of DCPD distillation with different storage time are given in Fig. 2.

To choose analytic signals NMR ^{1}H- spectra of distilled fractions were compared with spectra of pure samples of CPD and DCPD. Group of signals in regions 6,60...6,77; 6,53...6,60 and 3,01...3,20 ppm for CPD and in regions 6,00...6,18; 5,55...5,65 and 3,20...3,40 ppm for DCPD respectively were considered. The analysis of the spectra showed that the greatest errors may be made in regions of signal low intensities owing to overlapping mixture signals and products of further polymerization on the main signals of CPD and DCPD. Signals in the region from 3,01 to 3,40 ppm were excluded from analysis owing to reciprocal overlapping.

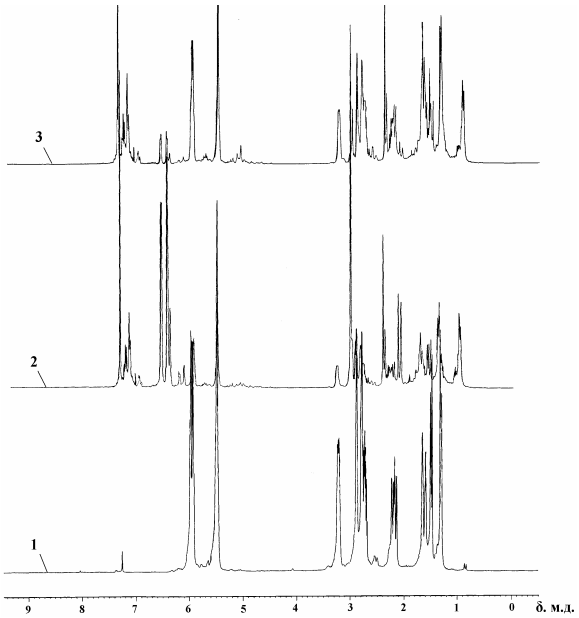

Fig. 2. *NMR ^{1}H-spectra: 1) DCPD of 96 % purity and 2, 3) DCPDF after distillation in 1 and 426 h. $C_{0\,CPD}$=27,9 wt. %*

Spectra measuring showed that in 426 h almost complete CPD dimerization occurs. Distillation conditions influence the ratio of the main monomers in fraction that is confirmed by the data of gas-liquid chromatography. Equilibrium between CPD and DCPD may be visually estimated and measured by changing integral intensities of typical proton signals.

For fractions with different content of CPD (Table 1), the dependences of changing intensities of selected signals are considered.

Concentration 40,0 wt. % (sample 1):

$I_{6,53...6,60}$=1,053·$I_{6,60...6,77}$ – 1,30; R^2=0,992;

$I_{5,55...5,65}$=1,189·$I_{6,00...6,18}$ – 1,82; R^2=0,999.

Concentration 27,9 wt. % (sample 2):

$I_{6,53...6,60}$=1,040·$I_{6,60...6,77}$ – 0,39; R^2=0,997;

$I_{5,55...5,65}$=1,204·$I_{6,00...6,18}$ – 1,34; R^2=0,998.

Values of coefficients close to unit at $I_{6,60...6,77}$ and at $I_{6,00...6,18}$ and high correlation coefficients indicate the fact that signals integral intensities of characteristic protons of CPD and DCPD change synchronously in studied time interval.

To calculate CPD and DCPD concentrations in distillation products the fraction with initial total DCPD and CPD concentration C_0=55,4 wt. % (sample 2) was used. The rating formula connecting DCPD concentration with signal intensities among themselves is given below:

$$C_{DCPD} = \frac{2 \cdot C_0}{\frac{I_{6,60...6,77}}{I_{6,00...6,18}} + 2}.$$

Results discussion

Typical curves of changing CPD and DCPD concentrations in fraction distillate within the time for the sample 2 are given in Fig. 3.

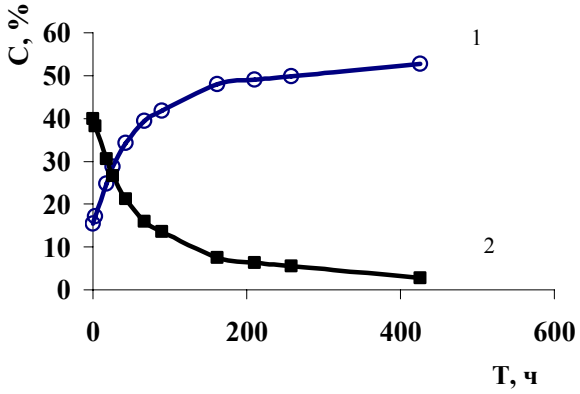

Fig. 3. *Dependence of changing DCPD (1) and CPD (2) concentrations on time*

Kinetic curves of CPD dimerization reaction are straitened in coordinates $1/C - T$ (Fig. 4) with correlation coefficients R^2=0,991. It indicates the fact that changing CPD concentration follows bimolecular law.

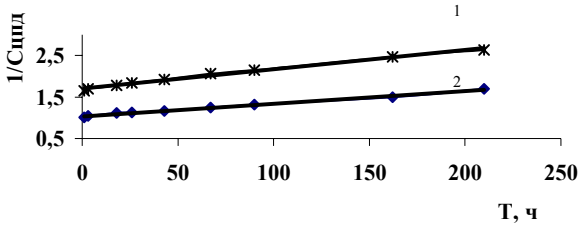

Fig. 4. *Kinetic curves of dimerization in distillate of dicyclopentadiene fraction with initial concentration of CPD, wt. %: 1) 27,9; 2) 40,0*

Rate constants of dimerization reaction determined by classic equation for second order reaction [14] are presented in Table 2.

Table 2. *Rate constants of CPD dimerization in distillate of dicyclopentadiene fraction, 10^{-4}·l/mole·h*

C_{0CPD}, %	Reaction time, h	
	0...43	0...209
40,0 Sample 1	14,5	20,7
27,9 Sample 2	12,8	15,4

In time interval 0...43 h for samples 1, 2 the rate constants of dimerization depend insignificantly on CPD initial concentration and rather close among themselves ($14{,}5\cdot10^{-4}$ and $12{,}8\cdot10^{-4}$ l/mole·h), however, substantially smaller than those determined before [7] for pure CPD ($20{,}2\cdot10^{-4}$ l/mole·h in interval 0...216 h).

Considering interval 0...209 h the rate constants change to $20{,}7\cdot10^{-4}$ and $15{,}4\cdot10^{-4}$ l/mole·h, respectively. The comparison of the obtained results with the data of the paper [7] in interval 0...209 h for sample 1 indicates good coincidence ($20{,}2\cdot10^{-4}$ and $20{,}7\cdot10^{-4}$ l/mole·h). The degree of CPD conversion in the paper [7] at duration in the interval 0...48 h is 42 %, in the given paper it is about 44 %; at duration of 216 h it is 94 %, we have at 209 h about 92 % that indicates the course of CPD dimerization reaction.

It should be noted that computational rate constants are dependent on initial CPD concentration and reaction time. At high conversion degrees (94 % and more, time 209 h) the rate constants depend on initial CPD concentration. For sample 1 the value $20{,}7\cdot10^{-4}$ is close to $20{,}2\cdot10^{-4}$ [8] however for sample 2 the dimerizaition constant is considerably lower – $15{,}4\cdot10^{-4}$.

Conclusions

The rate constants of CPD dimerization with initial concentration 40,0 and 27,9 wt. % in time intervals 0...43 and 0...209 h were calculated.

Studying the kinetics of CPD dimerization showed that greater value of reaction rate constant corresponds to higher initial concentration. The rate constant of the reaction also depends on conversion degree of CPD. Probably, the obtained data should be considered as the effect of errors at spectra measuring and using computational method of determining CPD and DCPD concentrations. In this connection concentrations should be measured and rate constants of CPD dimerization reactions should be computed at low degrees of monomer conversion. The calculated rate constants of CPD dimerization have a good fit with the results obtained in comparable conditions by other researchers.

Thus, in the given paper the process of CPD dimerization in composition of high-boiling fractions of LPP was firstly analyzed with the help of NMR ^{1}H-spectroscopy. The obtained results may be used for predicting properties of cyclo- and dicyclopentadiene containing technical fractions being a basic raw material for obtaining valued high-unsaturated oligomeric products.

REFERENCES

1. Mukhina T.N., Barabanov N.L., Babash S.E., Avrekh G.L. Pyrolysis of hydrocarbon raw-material. – Moscow: Khimiya, 1987. – 240 p.
2. Berents A.D., Vol-Epshtein A.B., Mukhina T.N., Avrekh G.L. Processing liquid products of pyrolysis. – Moscow: Khimiya, 1985. – 216 p.
3. Galimov Zh.F., Gibadullina Kh.M., Idrisova T.Sh. Preliminary treatment of raw-material as the method of improving the quality of petroleum polymeric drying oil // Khimiya i Tehnologiya Topliv i Masel. – 1994. – № 11–12. – P. 30.
4. Dumskiy Yu.V., No B.I., Cherednikova G.F., Belyakov M.E., Sherbakova L.Yu., Pokhmurskaya M.V., Gumenetskiy T.V. Obtaining clear petroleum polymeric resin of better quality from fraction C_9 of pyrolysis product // Neftepererabotka i Neftekhimiya. – 1994. – № 9. – P. 32–35.
5. Iwase Y.J. Color improvement of petroleum resin // Journal of Elastomers and Plastics. – 1979. – V. 11. – P. 307-316.

6. Dumskiy Yu.V. Petroleum polymeric resins. – Moscow: Khimiya, 1988. – 166 p.
7. Shuikin N.I., Naryshkina T.I. Kinetic studying dimerization reaction of cyclopentadiene // Zhurnal Fizicheskoy Khimii. – 1957. – V. 31. – Issue 2. – P. 493–497.
8. Fitere E.P., Bondaletov V.G., Bondaletova L.I. Polymerization of high-boiling fractions of pyrocondensate at catalyst systems of type Ziegler-Natta // Izvestiya Vuzov. Khimiya i Khimicheskaya Tekhnologiya.- 2004. – V. 47. – Issue 1. – P. 127–130.
9. Bondaletov V.G., Prikhodko S.I., Antonov I.G., Ermizin K.V., Kuznetsov N.N., Vakhrameeva O.V. Development of rational methods of obtaining oligomeric products of pyrolysis of the device EP-300 «Tomskneftekhim» // Plasticheskie Massy. – 2004. – № 5. – P. 48–50.
10. Fiterer E.P., Bondaletov V.G., Novikov S.S., Prikhodko S.I. Studying the interaction of some fractions of pyrocondensate with catalyst system $TiCl_4$-$Al(C_2H_5)_2Cl$ // Izvestiya Vuzov. Khimiya i Khimicheskaya Tekhnologiya. – 2004. – V. 47. – Issue 10. – P. 101–105.
11. Cyclopentodiene – new source of raw material for film-forming materials. Review information. – Moscow: NIITEHIM, 1986. – 39 p.
12. Timkin V.N., Lavrovskiy K.P., Brodskiy A.M., Rumyantsev A.N. Kinetics of dimerization of cyclopentadiene contained in benzene distillates of high-temperature pyrolysis of petroleum product // Neftekhimiya. – 1964. – V. 4. – № 3. – P. 435–439.
13. Lavrovskiy K.P., Rumyantsev A.N., Bulychev V.P. Kinetics of monomerization of cyclopentadiene codimers with isoprene and pyperilene // Neftekhimiya. – 1967. – V. 7. – № 1. – P. 46–50.
14. Emmanuel N.M., Knorre D.G. Course of chemical kinetics. – Moscow: Vysshaya Shkola, 1974. – 400 p.

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DETERMINING STRUCTURE OF PETROLIUM POLYMER RESINS OBTAINED ON THE BASIS OF HIGH-BOILING FRACTIONS OF PYROLYSIS LIQUID PRODUCTS

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On the basis of experimental spectra and spectra calculated with the help of ACDLabs (HNMR) NMR ^{1}H program the structure of petroleum polymer resins obtained by polymerization of high-boiling fractions of pyrolysis liquid products has been specified. Close fit between calculated and experimental results is obtained.

Using by-products and wastes of petroleum chemical manufactures decreases significantly the environmental load and may serve as a source of extra income at correct organization of technological process. At the present multipurpose utilization of raw material in petroleum refining industry is especially actual for saving unrenewable oil resources. Obtaining ethylene from virgin oil the quantity of the formed by-products – pyrolysis liquid products (PLP) – is comparable with end product output. The most valued products obtained from PLP are petroleum polymer resins (PPR) which can substitute more scarce and expensive materials on the basis of vegetable raw materials in manufacturing lacquers and paints.

Significant attention is given to the problems of PPR synthesis in scientific literature [1-4]. One of the main tasks of investigation is studying macromolecule structure that is connected with the necessity of synthesis of resins with specified property complex.

Studying high-molecular compounds determination of composition and structure of macromolecule, molecular weight of polymer chain and end group nature is of great importance. It is possible to obtain objective notion about the structure of high-molecular compound only by means of comparing data collected as a result of chemical and physical investigations; it is also possible to use efficiently computer programs for modeling compound structure and calculation of their NMR ^{1}H spectra.

The aim of the given paper is studying the structure of PPR synthesized by polymerization of various unlimited fractions of pyrolysis liquid products. Composition and properties of pyrolysis liquid products is determined to a considerable degree by raw material and conditions of pyrolysis which can often change in practice.

Two types of resins which were obtained by catalytic polymerization of high-boiling fractions of PLP: styrene fraction (SF) (PPR_{SF}) and dicyclopentadiene fraction (DCPDF) with boiling limits 130...190 °C (PPR_{DCPDF}) were chosen as the objects of investigation.

Experimental part

Resinous components formed as a result of oxidation and polymerization of unstable unlimited and diene hydrocarbons at PLP storage in plant conditions in the amount of 10,9 % for the first sample and 8,3 % for the second sample were separated from original fractions by atmospheric distillation up to 200 °C.

Quantitative identification of boiled away components of products of PLP processing was carried out by the method of gas-liquid chromatography at chromatographer LHM-80 with flame-ionization detector in steel capillary column of 15 m length, inner diameter 0,25 mm, stationary phase – apiezon *L*. Carrier gas is nitrogen, velocity is 80 ml/min, sample volume is 1 microliter.