

Heavy Pyrolysis Tar as a Raw Material for Hydrocarbon Resins

Zoriana Hnativ¹, Irena Nykulyshyn²,
Serhii Kozlov³, Oksana Khalaniia

¹Department of Chemical Engineering, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12,
E-mail: zoriana.y.hnativ@lpnu.ua

²Department of Organic Products Technology, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12,
E-mail: nk_iren@ukr.net

³Department of Chemical Engineering, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12

Abstract – Regularities of cooligomerization of C₉ fraction of diesel fuel pyrolysis and heavy pyrolysis tar with cationic polymerization catalyst - AlCl₃, have been investigated. The obtained cooligomer yield and physicochemical properties dependences on the C₉ fraction/heavy pyrolysis tar ratio and process conditions have been studied. The optimal conditions have been determined.

Key words – C₉ fraction; cationic cooligomerization; cooligomers; heavy pyrolysis tar; hydrocarbon resins; liquid pyrolysis products.

I. Introduction

The lower olefins (ethylene and propylene) production by pyrolysis of hydrocarbon raw materials is related to the problem of by-products utilization. Solving of this problem is an important technical-economic task. The liquid pyrolysis products (LPP) are main by-products, which are formed during gasoline and diesel fuel pyrolysis.

LPP is a mixture of various hydrocarbons, including aromatic hydrocarbons: benzene, naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, their methyl derivatives and other condensed aromatic hydrocarbons; acyclic and alicyclic dienes: isoprene, cyclopentadiene, piperylene etc.; vinylaromatic substances: styrene, methylstyrene etc.; indene and its alkyl derivatives, other olefins, as well as admixtures of paraffinic and naphthenic hydrocarbons. These liquid products are important raw material for organic synthesis [4].

LPP are divided into pyrolysis condensate – hydrocarbons mixture boiling off in temperature range 303–473K, and heavy pyrolysis tar (HPT) boiling off at temperatures above 473K [4]. Pyrolysis condensate most often is divided further into separate fractions with narrower boiling ranges: C₅ fraction (303–343K), C₆–C₈ fraction (343–423K) and C₉ fraction (423–473K).

Most of HPT hydrocarbons boil off at the temperatures above 473 K. However, due to the indistinctness of condensation HPT also contains some amount of hydrocarbons having final boiling point below 473 K. The composition of the HPT fraction, boiling off at the temperatures below 473 K, is similar to the pyrolysis condensate composition [4]. The HPT yield mainly depends on the feedstock fractional composition and the pyrolysis conditions [4, 6].

II. Experimental

Various substances with electron-seeking properties (Lewis acids) are used as cationic polymerization catalysts. Anhydrous AlCl₃ and catalytic complexes based on it are most widely used for hydrocarbon resins synthesis. Anhydrous aluminium chloride has the following advantages over another catalysts of liquid pyrolysis products polymerization: it is affordable, provides high product yield and high polymerization rate, enables using of pyrolysis products with broad boiling range as a raw material and the resins obtained with this catalyst has high softening point [2]. That is why we used this catalyst in our research.

Research object

Our research objects include: HPT, composition of which was determined in chromatographic study [3] and is given in table 1, and C₉ fraction of diesel fuel pyrolysis liquid products. Polymerizable components content in the C₉ fraction is about 60 % by wt. Main of them are styrene (≈ 19 wt %), dicyclopentadiene (≈ 18 wt %) and vinyltoluenes (≈ 8 wt %). Xylenes are main unpolymerizable component of the fraction [1, 4]. Anhydrous AlCl₃ was used as a catalyst.

The first stage of the research was aimed on the ascertainment of HR yield and properties dependences on C₉ fraction/HPT ratio and choosing of the optimal ratio. The experiments were carried out under the conditions having been determined to be optimal for C₉ fraction monomers cooligomerization with anhydrous AlCl₃: Ccat. = 2.5 % by wt, T = 373 K, τ = 3.5 h [1].

Yield is high at any value of C₉ fraction/HPT ratio. Anyway, there are two maximums: at 20 % and 70 % by wt. content of HPT.

To explain the above results let us consider the approximate composition of C₉ fraction and HPT. The yield of the product obtained from pure C₉ fraction indicates complete conversion of polymerizable hydrocarbons. Since HPT contains very few polymerizable compounds – only 5–6 % by wt., and C₉ fraction is main source of HR formation, decrease of C₉ fraction content in the reaction mixture should result in yield decrease. However, when raising the HPT content from 0 to 20 % by wt. the yield increases. Though HPT contains few polymerizable hydrocarbons, it contains 10–20 % by wt. resinous components [4] and 10–15 % by wt. heavy condensed aromatic compounds – asphaltenes [4], entering the HR composition as they are, without participation in polymerization process. The yield increase is obviously caused by this factor.

The increase of HPT content above 20 % by wt. leads to the resin yield decrease, because negative effect of C₉ fraction content reduction surpasses positive effect of presence of asphaltenes and resinous components of HPT. Besides cooligomerization, alkylation of aromatic, first of all naphthalenic (to a much lesser extent anthracenic and phenanthrenic) hydrocarbons by vinyl and indene monomers is also possible in the system, because, as is known, AlCl₃ is an effective alkylation catalyst.

So, the yield increase when raising HPT content over 50 % by wt. is, most probably, caused by alkylation

processes intensification. Less value of HR yield when using pure HPT as raw material may be explained by the lack of substances capable of reacting as an alkylating agent (content of such substances in HPT does not exceed 3 % by wt).

Bromine number of the HR is high in whole studied range of the feedstock compositions, and varies in relatively narrow range: 31.3–39.1 g Br₂/100 g. The most unsaturated product is obtained from pure C₉ fraction and from the mixture where C₉ fraction/HPT ratio is 50/50. The cooligomer obtained from C₉ fraction is highly unsaturated due to the presence of dicyclopentadiene (DCPD) units involving double bonds. Reduce of C₉ fraction content in the feedstock leads to decrease of the DCPD fragments content in HR resulting in HR bromine number decrease. However, unsaturation starts rising again when HPT content is raised above 30 % by wt. This is probably related to the unsaturation of the resinous compounds present in HPT composition, which affect the cooligomer bromine number when raising HPT content in the feedstock. At HPT content above 70 % by wt., the reactions of aromatic compounds alkylation with unsaturated substances prevail over other processes, and HR of lower unsaturation are consequently formed.

Average molecular weight and softening point of cooligomer decrease (fig. 1) when reducing the C₉ fraction/HPT ratio. Average molecular weight of the HR obtained from HPT is 487 only, while the HR obtained under the same conditions from C₉ fraction is characterized by molecular weight of 1094.

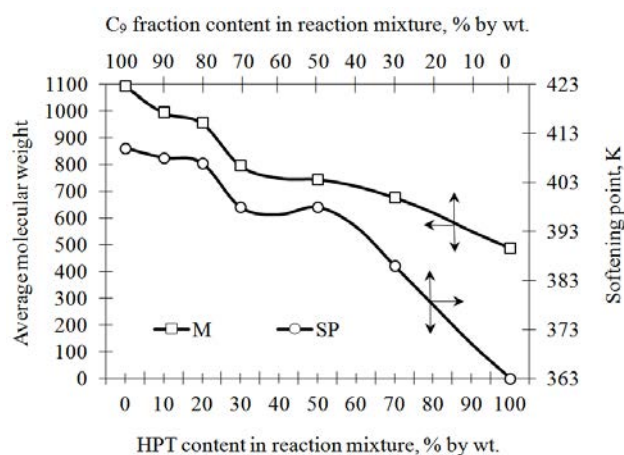


Fig. 1. Dependence of HR average molecular weight (M) and softening point (SP) on the HPT content in the feedstock (the rest is C₉ fraction) (AlCl₃, Ccat. = 2.5 % by wt, T = 373K, τ = 3.5 h)

Such regularities conform well to the conclusions made above when analyzing HR yield dependence on the feedstock composition. If HR is mostly a product of C₉ fraction polymerizable components polymerization, than it, obviously, has higher molecular weight compared to that of a resin consisting mostly of naphthalenic hydrocarbons alkylation products and resinous compounds present in the initial HPT.

Sharp decrease of HR softening point (sharper than corresponding decrease of molecular weight), when raising HPT content above 50% by wt., indicates the cooligomer nature change. At the HPT content below 50 % by wt., the resulting HR is mostly styrene-DCPD cooligomer with admixtures of asphaltenes and resinous components of HPT, while at the HPT content above 50 % by wt., the resulting HR mostly consists of the products of aromatic compounds alkylation with styrenic and indenic monomers, asphaltenes and resinous components of HPT. The highest HR yield is achieved at the C₉ fraction/HPT ratio equal to 30/70 (69.4 %) and somewhat less (66.9 %) at 80/20. However, HR molecular weight is considerably higher at the C₉ fraction/HPT ratio = 80/20 (957 compared to 677 at 30/70). Consequently, softening point is higher as well (407 K compared to 386 K at 30/70). HR bromine number varies in relatively narrow range (31.3–39.1 g Br₂/100 g), so it cannot be an optimality criterion. Based on the foregoing discussion the C₉ fraction/HPT ratio equal to 80/20 is considered to be the optimal ratio. Further research is aimed on the ascertainment of optimal conditions of HR synthesis from the C₉ fraction and HPT mixture at the optimal ratio.

Conclusion

Based on the research done the regularities of cooligomerization of C₉ fraction and HPT of liquid pyrolysis products catalyzed by AlCl₃ have been ascertained. It has been determined how the product yield and properties depend on the C₉ fraction/HPT ratio. The optimum C₉ fraction/HPT ratio in terms of HR yield and properties has been determined to be equal 80/20. Study of HR synthesis from such mixture under various conditions allowed as to choose the optimum cooligomerization conditions, which are as follows: the catalyst concentration – 2.5 % by wt, duration – 2 h., temperature – 373 K.

The HR obtained at these conditions are characterized by the yield – 65.0 %, average molecular weight – 967, softening point – 395 K and bromine number – 48.6 g Br₂/100 g.

References

- [1] Study of catalytic polymerization of C₉ fraction / Y.M. Mokryy, I.Y. Nykulyshyn, B.I. Budzan // *Dopovidi NAN Ukrainy*, 1994. No. 5. – P. 134-139 (in Ukrainian).
- [2] K. Naumburg // *Petroleum and Coal*, 1968. V. 10, No. 2. – P. 69-77 (in Czech).
- [3] Chromatographic determination of chemical composition of heavy pyrolysis tar / M.A. Lebedeva, V.D. Kolesnyk, V.I. Mashukov, A.V. Yegorov // *Izvestiya Tomskogo Politehnicheskogo Universiteta*, 2010. V. 316, No. 3. – P. 102-105 (in Russian).
- [4] Processing of liquid products of pyrolysis / A.D. Berents, A.B. Vol-Epshtein, T.M. Mukhina, G.L. Averkh. – Moscow, Khimiya, 1987. – 240 p. (in Russian).