INNOVATIVE PERSPECTIVES OF USING HEAVY PYROLYSIS RESIN

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ABSTRACT. Thermal gas-phase pyrolysis of hydrocarbon raw materials in pipe furnaces remains to be the main strategic process of ethylene and propylene production. Nowadays, the possibility of the pyrolysis process intensification to increase the target product yield draws attention of scientists. But besides the olefins (target products) the pyrolysis process is the source of heavy pyrolysis pitch. Considerable development of petrochemical industry requires finding new applications of the by-products from pyrolysis gas and liquid pyrolysis products. Nowadays, environmental safety considerably deteriorates because of great volume and high increasing rate of ethylene production. Reasonability of the industrial wastes – heavy pitch of pyrolysis – using as a component of the feedstock in synthetic petroleum resins production is asserted. This improves production efficiency of petrochemical plants and decreases environmental effects.

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 alkylderivatives, other olefins, as well as admixtures of paraffinic and naphthenic hydrocarbons. These liquid products are important raw material for organic synthesis [1].

LPP are divided into pyrolysis condensate - hydrocarbons mixture boiling off in temperature range 303-473 K, and heavy pyrolysis tar (HPT) boiling off at temperatures above 473 K [1]. Pyrolysis condensate most often is divided further into separate fractions with narrower boiling ranges: C_5 fraction (303-343K), C_6-C_8 fraction (343-423 K) and C_9 fraction (423-473 K). 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 [2, 3]. The HPT yield mainly depends on the feedstock fractional composition and the pyrolysis conditions [1-3]. C_5 and C_9 fractions contain considerable amount of polymerizable hydrocarbons and consequently are used to produce cooligomers of aliphatic and aromatic nature, respectively. These cooligomers are called hydrocarbon resins (HR).

Unfortunately, today there isn`t technology that would allow the full use of all the valuable components of the HPT. While the processes of production of petroleum polymer resins (PPR) based on reactive unsaturated hydrocarbons of pyrocondensate and light pyrolysis resins are realized in industry. This is due to the availability of raw materials and low operating costs, the possibility of widespread use of petroleum polymer resins in paints, paper, tire, rubber and other areas of industry in which they successfully replace vegetable oils, rosin, albumin and other products of natural origin.

Low sulfur content makes it possible to obtain from the ecological point of view pyrolysis resins of low-sulfur carbonaceous composite materials. HPT practically does not contain heterocyclic compounds, which distinguishes it favorably from the coking coal of resin. Therefore, its processing does not require complex technical solutions and costly technological

**Dependence of yield and physical and chemical indices of DPPR
on the factors of the process**

Terms of the process / Factors	Yield DPPR, % wt.	Bromine number DPPR, g Br_2/100 g	Mol.Wt. DPPR	T_p DPPR, K
Duration of the process – 1 h., $C_{cat.}$ – 1,0 % wt.				
Catalyst - $TiCl_4$				
T=333 K	56,0	42,3	720	370
T=353 K	57,1	44,7	680	360
T=373 K	59,4	45,9	650	359
T=393 K	56,0	49,5	640	356
Catalyst - $AlCl_3$: EA : KC				
T=333 K	53,2	48,9	610	364
T=353 K	55,1	48,5	570	355
T= 373 K	57,0	47,0	560	350
T=393 K	59,8	47,9	520	346
Temperature of the process – 373 K, $C_{cat.}$ – 1,0 % wt.				
Catalyst - $TiCl_4$				
τ = 1 h.	59,4	45,9	650	359
τ =2 h.	59,6	44,6	640	358
τ =3,5 h.	59,7	45,9	650	359
Catalyst - $AlCl_3$: EA : KC				
τ = 1 h.	57,0	47,0	560	350
τ = 2 h.	59,4	45,3	510	353
τ = 3,5 h.	58,7	46,4	490	352
Temperature of the process – 373 K, τ =3,5 h.				
Catalyst - $TiCl_4$				
$C_{cat.}$ – 0,5 % wt.	53,1	47,6	700	363
$C_{cat.}$ – 1,0 % wt.	59,7	45,9	650	359
$C_{cat.}$ – 2,5 % wt.	58,6	43,8	460	357
Catalyst - $AlCl_3$: EA : KC				
$C_{cat.}$ – 0,5 % wt.	48,2	53,1	760	352
$C_{cat.}$ – 1,0 % wt.	58,7	46,4	490	352
$C_{cat.}$ – 2,5 % wt.	58,5	44,9	600	351

operations associated with the purification of resin from sulfur, nitrogen and oxygen-containing compounds. At present, practical implementation on an industrial scale has found the following directions of the use of heavy pyrolysis resin as: raw materials for the production of carbon black, for the process of coking, the production of naphthalene; component of boiler fuel for installations of different purposes; fuel oil component; in asphalt-bitumen compositions; superplasticizer concrete; in the production of pyroplast (an analogue of styrenic-indene resins) [2, 4-8]. In addition, a trend of weighting of pyrolysis raw material is observed because heavy oil mixtures are involved in processing (gas-oil stock, black oil, oil tar), which causes an increase in the yield of HPT. This fact defines the necessity to process HPT into commercial products.

The main threatening areas of harmful action of pyrolysis resin on the environment are pollution of the atmosphere, water bodies and soil due to emissions, leakage, violation of storage rules, emergency situations. One of the negative effects of the HPT on the environment is their burial and burning.

The heavy pyrolysis resin contains condensed aromatic hydrocarbons with alkyl substituents (20.24% wt.), oligomers of alkenylaromatic hydrocarbons, asphaltenes, and others. Significant content of aromatic hydrocarbons and a high value of the bromine number (64.4 g Br_2/100 g) indicate the tendency of heavy pyrolysis resins to compaction reactions (condensation, polymerization, co-oligomerization).

The share of heavy pyrolysis tar (HPT), a related product of petrochemical production, varies from 3-4 to 40% [1]. The urgency of issues of increasing the environmental safety of the pyrolysis process is aggravated by the large scale and pace of capacity building of ethylene production and the tendency to use "heavier" raw materials. Therefore, it is important to develop a technology that would allow rational processing of heavy pyrolysis resin into valuable products. The regularities of the production of dark petroleum polymer resin (DPPR) based on heavy pyrolysis resin were studied in the presence of homogeneous catalysts - titanium tetrachloride and catalyst complex $AlCl_3$: EA(ethylacetate): KS(ksylene).

Increasing the concentration of homogeneous catalysts up to 2.5% wt. leads to a decrease in the molecular weight of the resulting resins throughout the studied range of temperatures (Table 1). The bromine number of synthesized DPPR is high (44.9 ... 53.1 g Br_2/100 g, table 1). In the presence of titanium tetrachloride, the co-oligomerization occurs by the mechanism of sequential reactions. In the initial reaction period, the cooligomerization of the most active unsaturated compounds is observed (yield of DPPR - 59.4% wt.). In the following, the induction period and the cooligomerization of less active compounds were noted. The yield of DPPR increases by only 0.3% wt. within the next 2.5 hours. the process. The color index of synthesized products is extremely high (over 2600 mg I_2/100 cm^3). This is typical for this raw material. Optimal conditions: catalyst concentration 1.0% wt. and the temperature of the cooligomerization of 373 K. It was found that to conduct cooligomerization over 2 hours inappropriate. Under these conditions, the yield of DPPR is high (59.6% wt. for $TiCl_4$ and 59.4% wt. for KK).

For comparison, the heavy pyrolysis resin (HPR) cooligomerization was carried out under similar conditions by a thermal process (T = 373 K) without the use of a catalyst. PPR was obtained with a significantly lower yield (44.2% wt.). Their characteristics are worse: the bromine number is 47.3 g Br_2/100 g, the molecular weight is 425, the softening temperature is 354 K.

It has been established that in the presence of Lewis acids, condensation processes of aromatic compounds may occur in the system. The heavy pyrolysis resin contains a significant amount of naphthalene and its derivatives (20.25% wt.). The products of their condensation are structures (I - IV).
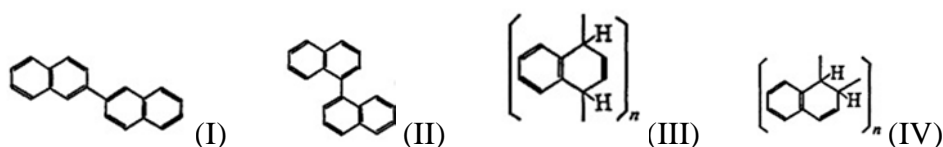
A heavy pyrolysis resin is difficult to process individually. Therefore, the process of co-oligomerisation of a mixture of hydrocarbons of fraction C_9 and HPR components using a homogeneous catalytic complex ($AlCl_3$: EA: KC) was investigated.

The increase in temperature and duration of the reaction positively affects the course of co-oligomerization. The yield of cooligomeric dark petroleum polymer resins (CDPPR) is increasing. Their bromine number decreases (table 2). The ratio [fraction C_9]: [HPR] is 80:20 (% wt.). With an increase in the temperature of the process, the yield (38.1-49.8% wt.) increases and the molecular weight of the CDPPR (970-780) decreases. The high temperature of softening of the cooligomeric dark oil-polymer resins (393-386 K) is an important characteristic for further use of

this type of products in the oil-polymer-bitumen compositions. It is noted that the catalytic processes of increasing the yield and decreasing the molecular mass of the cooligomers are characteristic. It has been established that in the range of catalyst concentrations 0.5 ... 1.0% wt. the yield of CDPPR increased from 46.3 to 49.5% wt. The resulting resins are characterized by a high temperature softening (387-388 K). Further growth of the concentration of the catalytic complex does not lead to a significant increase in the output of the CDPPR while reducing the temperature of softening the resin.

Table 2

**Dependence of yield and physicochemical indices of CDPPR
on process factors (AlCl$_3$: EA: KS; [Fraction C$_9$]: [HPR] = 80: 20 (% wt.))**

Terms of the process / Factors	Yield CDPPR, % wt.	Bromine number CDPPR, g Br$_2$/100 g	Mol.Wt. CDPPR	T$_p$. CDPPR, K
C$_{cat.}$= 1,0 % wt., τ = 3,5 h.				
T=353 K	38,1	58,0	970	393
T=363 K	41,1	57,1	810	391
T=373 K	49,5	56,6	790	388
T=393 K	49,8	54,9	780	386
Temperature of the process – 373 K, C$_{cat.}$=1,0 % wt.				
τ = 0,5 h.	33,49	59,1	670	375
τ = 1,5 h.	38,6	58,7	680	378
τ = 2,0 h.	44,0	57,4	700	379
τ = 2,5 h.	48,2	57,0	730	383
τ = 3,5 h.	49,5	56,6	790	388
Temperature of the process – 373 K, τ = 3,5 h.				
C$_{cat.}$= 0,5 % wt.	46,3	57,2	800	387
C$_{cat.}$= 1,0 % wt.	49,5	56,6	790	388
C$_{cat.}$= 2,0 % wt.	49,7	53,9	770	381
C$_{cat.}$= 2,5 % wt.	48,9	50,6	760	377

The optimal technological parameters of the process of synthesis of CDPPR are determined: temperature - 373 K, duration of the process - 3.5 hours, concentration of the catalytic complex - 1.0% wt. Synthesized copolymer dark petroleum polymer resins can be used: in the production of waterproofing materials for increasing the adhesion of the adhesive base, its thermal stability, ductility; as an adhesion addition to road bitumen; in the manufacture of concrete for increasing frost resistance, reducing the formation of cracks and hygroscopicity; in paint and varnish products to improve adhesion, film formation.

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