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Review article

Improving the efficiency of high-temperature processes for producing lower olefins via deep-processing of by-products

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Abstract

Processes for producing lower olefins are critically examined. It is noted that pyrolysis of various types of hydrocarbon is still the main process of obtaining ethylene and propylene, and is accompanied by the formation of considerable amounts of by-products, such as liquid pyrolysis products. We present an analysis of domestic and foreign scientific, technical, and patent information pertaining to the rational use of petrochemical production by-products, aimed at obtaining hydrocarbon (petroleum) resins. We consider the raw materials involved in obtaining the resins, and generalize data on existing methods of obtaining resins using thermal, initiated, and ion (catalyst) polymerization.

1. Current status and trends in ethylene and propylene technology

Production of lower olefins is developing at an accelerated pace all over the world. Ethylene and propylene are the raw materials of various monomers: ethylene and propylene oxides; acrylonitrile, acrylamide; styrene, α-methyl styrene; vinyl chloride, vinyl acetate and many other valuable compounds [1]. But the main focus for the use of ethylene and propylene is obtaining polyethylene and polypropylene using different technologies. At the same time, production of ethylene and propylene copolymers, and ethylene-propylene-diene rubber having unique physical, chemical, and physio-mechanical properties, is also developing at a rapid pace. Currently, one of the methods for obtaining ethylene and propylene is hydrocarbon pyrolysis [2]. A review of major developments in the area of propylene production is presented in Reference [3].

All over the world, the most popular pyrolysis raw material for producing lower olefins is straight-run gasoline (naphtha). However, the gradual exhaustion of light sweet crudes leads to changes and diversification of the structure of the raw materials used during pyrolysis [4,5]. A higher level of refining can be achieved by ballasting pyrolysis raw materials using low-demand mazut and tar. On the other hand, the necessity of their use requires new technical solutions. These solutions are associated with changes to the structure of pyrolysis furnaces, quenching systems and produce separation [6]. The inevitable increase of aromatic compounds content in pyrolysis by-products forces researchers to devote their attention to different areas: reducing the amount of highly aromatic compounds by decreasing the exposure time or by using reactive diluents that are also high-temperature heat transfer fluids; qualified separation of pyrolysis products [4].

With increasing production of natural gas and gas separation efficiency, using ethane and propane to produce ethylene and propylene in the process of catalytic dehydrogenation becomes logical [4,7]. Currently, about 25% of the world's ethylene and propylene is produced using this method. Undoubtedly, this method is the most economic, due to the low cost of the raw materials, minimum consumption of raw materials and energy per unit of production, low yields and the ease of separating pyrolysis gas from by-products. However, the content of ethane and propane in natural gas is relatively low (2–20%), and only slightly higher in associated gas (up to 40%), and therefore the possibility of using the main component of natural gas – methane is constantly sought after [8]. There are two problems with direct thermal pyrolysis of methane: high energy costs and low yield of the desired product. The use of catalytic

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systems does not have a significant impact on the situation. The direct conversion of methane into alkenes via an oxidative condensation process is constantly being considered, but so far there are no practical solutions.

Alternative approaches to using primarily methane natural gas include multistage processes through methanol [9] or methyl chloride [10].

The proposed variants "through methanol" are based on vapor and/or carbon dioxide conversion of methane in order to obtain syngas, which can then be converted into methanol, which is catalytically pyrolyzed at temperatures 400–500 °C on zeolites such as ZSM or SAPO. The use of different catalyst systems allows us to produce both ethylene and propylene. The widespread adoption of these processes is also limited by the significant power consumption, and the need to implement a number of steps during the process of synthesis and separation (purification).

The disadvantages of obtaining lower olefins "through methanol" led to the emergence of similar technological methods. Reference [11] discusses the process of obtaining ethylene and propylene "through methyl chloride," wherein the first stage involves the initiated chlorination of methane. The second stage is technically similar to catalytic pyrolysis of methanol and is performed on the same catalysts. The advantage of the proposed method is the fact that unlike methanol, methyl chloride is produced in one step. The pyrolysis of methylene chloride can be implemented in a stationary catalyst bed, and in a fluidization mode. The resulting polychlorinated products are subjected to catalytic dehydrochlorination with the regeneration of the initial hydrocarbon and hydrogen chloride. The developers of this technology note that the processing conditions are milder, but that the hardware requirements are more stringent than that of the methanol process [12].

Recently, there has been renewed interest in using catalytic dehydration of ethanol to produce ethylene on an industrial scale [13]. Modern alumina-based catalysts ensure a high 92–97% yield of ethylene at temperatures 400–450 °C.

A metathesis reaction can be used to increase the ethylene yield by employing the by-products (higher α-olefin) released during the pyrolysis [14,15]. This reaction can also be useful in balancing ethylene and propylene products, for example during the dimerization of ethylene to 1-butane, followed by its isomerization to 2-butane and co-metathesis with ethylene; we get propylene with a quantitative yield [16]. However, the most adequate method of obtaining lower olefins can be implemented as an addition to the existing techniques used to reduce the yield of by-products (higher α-olefins) released during primary production.

Despite the relative diversity of methods used to synthesize lower olefins, hydrocarbon pyrolysis is the method with the most technological value. This is associated with the fact that there is an existing stability in the flow of raw materials, as well as the availability of equipment required to prepare the raw materials, implement the target process, separate the products, and skillfully use the secondary products.

Catalytic pyrolysis [17] is presented by many researchers as an alternative to the thermal pyrolysis of hydrocarbons. The transition to this process is possible with minimum hassle. The possibility of transferring the pyrolysis furnace from the thermal to the catalytic mode was examined as far back as 1991 [18]. These results allowed us to recommend catalytic pyrolysis for adoption in order to increase the yield of lower olefins, reduce coking and formation of by-products, reducing the temperature and pressure of the main process, increasing the yield of aromatics. Expanding the range of catalysts, adapting them to different kinds of raw material, increasing the activity and reducing the cost of production are the main problems that are to be solved in the development of new catalytic systems. Catalysts based on vanadium oxide, strontium [19], and iron [20] are proposed.

In comparison with thermal pyrolysis, olefin yield is increased by 27% when we use the catalyst ZVN-2, based on zeolite ZVN – foreign analogue ZSM-5 (60 %) and aluminum oxide (40 %), obtained via pyrolysis of straight-run gasoline in the presence of steam at a temperature of 650 °C [21]. The way in which the ratio of steam: raw materials influences the yield of the desired products during the pyrolysis of the propane-butane fraction in the presence of ZVN zeolites, is examined in Reference [22]. The optimal ratio turned out to be 0.2:1, and if the ratio is increased to 0.6:1, we have an almost two-fold reduction in the yield of the desired products. When evaluating the way in which steam affects the pyrolysis process of heavy oil (Chinese Daqing Factory) in a fluidized bed in the presence of catalyst CEP-1 (used for CPP technology) [23], we came to the conclusion that in addition to mixing and diluting, the steam also inhibits the hydrogen transfer, aromatization, polymerization reactions, and accelerates the gasification of the coke being formed, while maintaining the catalyst activity [23,24]. The catalytic cracking of vacuum gas oil in an upstream catalyst stream ZSM-5, described in Reference [25], corresponds to the best foreign analogs in terms of performance.

Recently, the use of nanoparticles has been prevalent in the research pertaining to catalyst systems of hydrocarbon pyrolysis [26]. These particles turned out to be much more active than existing industrial catalysts.

When studying the catalytic activity of ultrafine particles, obtained via electro explosive dispersion of metal and bimetal conductors from Ag, Al, Cu, Fe, Ni, Ti, Pt, W, Mo, and deposited on the inner surface of the quartz and ceramic tubes, a multitude of catalytic activity for ethylene yield, total olefin yield and coke formation was obtained [27]. The comparison of reactor materials showed that the use of a metal reactor leads to an increased deposition of coke on the reactor walls, versus the quartz and ceramic reactors. For some metals (Fe, W), a repeat pyrolysis after 6 months leads to a decrease in the yield of ethylene and propylene, and a significant increase in coke yield [27].

Therefore, the majority of real developments of the lower olefins production currently relate to thermal pyrolysis. These can be divided into the following: development of new construction materials and changes to the design of the individual components of the reactor equipment with an increase in the "rigidity" of the process; separate heat treatment of the individual fractions and their subsequent pyrolysis during

the ballasting of the raw materials; high-energy processing of raw materials, catalyst, and water vapor; the use of additives that increase the overall yield of the desired product and changing the ethylene–propylene ratio, reducing coke formation; organizing the recycling of fractions of pyrolysis by-products; organizing the process of separating the pyrolysis products in order to minimize losses; obtaining new products based on pyrolysis by-products.

The optimization of the pyrolysis processes in order to create greater "rigidity" has almost reached its limit due to the fact that pyrolysis pipes lose their strength at temperatures above 1200 °C. The burner designs that are currently in development have not reached their "ceiling" due to the possibility of using hydrogen and acetylene fuel burner designs, creating burner structures out of refractory ceramic materials, and supplying fuel at a supersonic speed. Progress in the area of improving designs is aimed at increasing the ratio of "surface heat": "reaction volume," which allows achievement of a higher processing temperature at the same wall temperature. Increasing the equilibrium concentration of ethylene and propylene at the outlet of the furnace is achieved by rapid movement of the reaction mass to the quenching-evaporation unit with a maximum reduction of hydraulic flow resistance and a rapid quenching of pyrolysis [28].

References [29–31] by V.I. Erofeev, present the results of processing the internal surfaces of the pyro coils during pre-pyrolysis of gasoline. This procedure leads to the deactivation of the most active metal centers, the formation of amorphous coke, higher yield of the desired lower olefins, and an increase in the ipso path. The process of inhibiting the metal pyrolysis furnace surface using microscopic quantities of palladium black is an independent focus in terms of improving the pyrolysis process [32].

In order to process heavy raw materials, intermediate selection of the volatile part of hydrolyzed materials is proposed [33]; cracking it in the convection zone and supplying it to a radiation zone, in the main current. The author of Reference [33] considers that this technique allows processing any heavy raw material.

There are many research attempts at the lab level, to use the different types of high-energy radiation in order to control the pyrolysis process. Reference [34] discusses the different approaches related to processing the steam using microwave radiation directly before feeding it into the pyrolysis oven. Based on the obtained results, the authors have concluded the following, with regards to the intensification of the pyrolysis of the gasoline fraction: increase the ethylene and propylene output, reduce the amount of generated pyrolysis resins. Pyrolysis of the propane-butane fraction under these conditions also leads to better performance. The authors of Reference [35] would like to note that the use of microwave radiation for pre-treatment of the steam-diluent increases the yield of unsaturated hydrocarbons by more than 10%. A similar effect is achieved during the microwave-processing of technical water containing salts or metal oxides [36].

Lab studies of the nitrogen plasma impact on gas condensates have shown that there is a possibility of obtaining acetylene, ethylene, and propylene with a total content of about 24 vol. % [37], whereas plasma treatment of sludge in the presence of catalysts yields products containing 24% acetylene and 20% ethylene [38].

A lot of work is carried out with the focus of improving the process of thermal pyrolysis, to be achieved with bare minimum changes to existing technologies. One such approach is the use of initiating agents, such as atomic and molecular hydrogen. Under these conditions, regardless of any slight reductions in the yield of propylene and butadiene-1,3, the total yield of low olefins increases along with a significant reduction in coke formation [39,40]. The economic aspects of replacing water vapor with hydrogen are considered in References [41–43], wherein there is a decrease in the efficiency of the pyrolysis installation when water is replaced with hydrogen. Increasing ethylene yield by 10% facilitates having an initial pyrolysis in the presence of allene, emitted from the propane-propylene fraction [44].

Therefore, the pyrolysis of different types of hydrocarbons is currently the leading method for obtaining lower olefins, and is accompanied by the formation of a significant amount (20–40%) of side product liquid.

Skilled use of the pyrolysis by-products significantly affects the cost of the basic products and products of deeper processing. By-products are considered to be rich raw materials that can be used in the production of various chemical compounds: benzene, toluene, xylene, styrene, naphthalene, cyclopentadiene, cyclopentene, isoprene, piperylene, pentenes, high-quality carbon black, and others. The processes of producing chemical products from pyrolysis resin are successfully conquered using traditional methods of preparation using raw material coke. The cost-effectiveness and appropriateness of using pyrolysis resin to isolate individual components depends on the power of the processing plants, which, in turn, depends on the individual capacities of the ethylene-propylene units and the possibility of cooperating on any productions that are either geographically or economically separated.

At present, in Russia it is both necessary and possible to produce new products based on existing industry, thus combining the large-capacity and high-tech chemistry [45,46]. Variants of complex processing schemes of liquid pyrolysis products provide for the allocation and use of large components or the re-processing of whole fractions into limited numbers of products with reproducible physical, chemical, and technical characteristics [47,48].

Fractions of pyrolysis resin that are the richest in unsaturated hydrocarbons (styrene, vinyl toluene, indene, etc.) can generally be used to produce petroleum resins [49–51], which are valuable products that can be used to reduce the consumption of expensive and scarce natural resources: vegetable oil, rosin, wood-pyrogenic and indene-coumarone resins [45,52–57]. Petroleum resins are used for various industries: paint, cellulose paper, building and road construction, rubber and tire, wood and furniture. In addition, resins can be used for quick-drying, pore-filling materials in painting and decorating, adhesives and waterproofing materials.

2. By-products of pyrolysis: their brief classification and characteristics (fractional and component composition), methods of recycling different fractions of pyrolysis by-products

Pyrolysis by-products (liquid pyrolysis products) are subdivided in accordance with their boiling temperature, into mild pyrolysis resin (pyrocondensate, pyrobenzene) boiling at up to 190–200 °C, and heavy pyrolysis resin, which boils at 190–200 to 360 °C. An important indicator that influences the way the pyrolysis resin is processed, is the iodine number that ranges from 25 (hard resin) to 130 g I_2/100 g (fraction C_5 of mild pyrolysis resin) [58].

The implemented industrial processes involve the selection of the following fractions from mild pyrolysis resin: C_5, benzene-toluene-xylene (C_6-C_8) or benzene-toluene, C_9; whereas the heavy pyrolysis resin is separated into naphthalene concentrate, alkyl naphthalene, acenaphthene, fluorine and anthracene-phenanthrene fractions.

Depending on the type of raw material and pyrolysis conditions, the yield and composition of the pyrolysis products will vary significantly (Table 1) [58]. Thus, during the pyrolysis of gas oil, versus pyrolysis of gaseous hydrocarbons and benzene, we get a sharp increase in the output of liquid products, primarily heavy tar, whereas in mild pyrolysis resin we get a decrease in aromatic content.

The main areas of how liquid pyrolysis products are processed are presented below.

- Shallow hydrogenation of unsaturated hydrocarbons using hydrogenation, as components of high-octane motor fuel [59–65]. This method is currently limited by benzene content requirements, and the total content of aromatic hydrocarbons in gasoline [66]. Variants of technological flowsheets for hydrogenating liquid pyrolysis products are available in Reference [67]. The first version is reduced to a pre-separation of fraction C_6-C_8, its hydrogenation, and further joint use with fraction C_9 as motor fuel components. The second option involves the hydrogenational purification of the entire fraction C_5-C_9 followed by the separation of fraction C_9 and using it to produce gasoline.
- Shallow hydrogenation of unsaturated hydrocarbons combined with hydrodealkylation [68–72] and the use of hydrogenate as a raw material, for example benzene to be used

for cyclohexane, cyclohexanone, and subsequently for the preparation of caprolactam.

- The complex processing of liquid pyrolysis products using physical methods of separation (distillation, rectification, including azeotropic, adsorption and absorption), leading to the production of a broad range of customized products. The proposed schemes [45,49] are very similar and have a declarative nature in terms of the complexity of their actual implementation and high capital costs.
- Thermal processing in order to obtain technical carbon (soot), to be used in the production of rubber products, tire and paint industry, road construction.
- Polymerizational purification of liquid pyrolysis products in order to produce a solvent, nephras, and individual aromatic solvents (benzene, toluene, xylene).
- Polymerization of unsaturated hydrocarbons from liquid pyrolysis products in order to obtain petroleum resins [45]. We must note that since complex mixtures of unsaturated hydrocarbons (monomers) and non-polymerizable hydrocarbons are used as a raw material in the synthesis of resins, we pretty much get copolymerization in the solution. Given that the molecular weight of resin is typically no more than 3000, the process should be examined as co-oligomerization. In this embodiment, unlike the previous case, the resin is the desired product, and the resulting solvent or individual solvents are the by-products having intrinsic value. Further hydrogenation of resin is possible [73]. Raw material resources for resins can be increased due to the use of highly unsaturated products of cracking heavier types of raw oil materials – mazut, tar, petrolatum, petrochemical production waste.

2.1. Mild pyrolysis resin is the raw material used to obtain PRs

Fractions C_5 and C_9 are the main components in the production of mild petroleum resin. The composition of the fractions varies broadly, depending on the initial raw materials and the pyrolysis conditions. Fraction C_5, which boils between 30 and 70 °C, contains linear, cyclo-, and branched pentenes, as well as a significant number of different diene hydrocarbons: isoprene, cyclopentadiene, *cis*-, *trans*-pentadiene- 1.3.

Fraction C_8-C_9, which boils between 120 to 190 °C, has concentrated alkenyl aromatic hydrocarbons and

Table 1
The yield of some pyrolysis products of various raw materials on ethylene installations [58].

| Pyrolysis products	The yield of pyrolysis products of various raw materials, %						
	Ethane	Propane	*n*-Butane	Benzene		Gasoil	
				Mild	Medium	Atmospheric	Vacuum
Ethylene	52.0	37.0	31.0	29.8	27.1	23.5	19.0
Fraction C_5, incl.:	0.8	2.8	4.0	5.3	4.9	3.4	2.8
Cyclopentadiene	0.1	0.5	0.7	1.5	1.5	1.5	2.0
Cyclopentane	0.1	0.4	0.4	1.3	1.4	–	–
Fraction C_6-C_{10}	1.3	4.4	7.4	12.7	15.5	12.4	11.7
Heavy resin	0.02	0.05	1.1	4.0	5.0	19.2	25.0

dicyclopentadiene (%): 5–18 styrene, 2–6 α-methyl styrene, 2–4 β-methyl styrene, 5–13 dicyclopentadiene, 10–15 vinyl toluene, 6–10 indene [49].

The content of unsaturated hydrocarbons, dienes in particular, varies rather significantly, which is explained by the differences in the composition of the raw materials and the pyrolysis conditions, as well as the methods behind the selection and storage of the fractions. Thus, the content of alkenyl monomers and dicyclopentadiene in the fraction C_9 (130–190 °C) of the pyrocondensate obtained during the pyrolysis of gasoline in the propylene mode, is 49.4%, whereas under more rigid pyrolysis conditions it increases to 60.8% [45]. As the temperature of pyrolysis gasoline increases from 775 to 840 °C, we see an increase in the content of alkenylaromatic hydrocarbon such as styrene, α-methylstyrene, indene, vinyltoluene, and dicyclopentadiene.

This study discusses the possibility of using fractions of liquid pyrolysis products derived from furnaces SRT-IV Company ABB Lummus Global. The depentanizer column of such a setting can operate in different modes without compromising the basic process: it can function in the project depentanization mode and the hydrogenation product selection mode [74,75]. By varying the reflux ratio and the bottom and top temperatures of the depentanizer column, we can obtain the still bottoms with different contents of styrene and dicyclopentadiene (Table 2): styrene fraction (SF), which is close in composition to the fraction C_9, dicyclopentadiene fraction (DF1, DF2) [76]. Thus, by increasing the top temperature to 150–160 °C, we get products that mainly include high-boiling monomers: dicyclopentadiene, dimethyl dicyclopentadiene, indene (Table 2, Fractions DF1, DF2).

The implementation of technology that allows us to produce petroleum resins from the bottom stills of a depentanizer column first of all requires their distillation or rectification in order to remove any original additives, inhibitors, or products of oxidation and gumming. In this case, the dicyclopentadiene that is part of the fractions decomposes, forming cyclopentadiene, which is extremely reactive [77]. When storing this type of fraction, the cyclopentadiene, which is both a diene and a dienophile, enters into a reversible dimerization reaction, in accordance with the Diels-Alder mechanism:
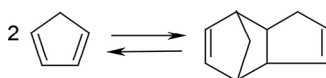
The concentration of cyclopentadiene and its ratio to other monomers often determines the reactivity of the fraction. Obviously, the degree of decomposition of dicyclopentadiene is determined by the distillation or rectification mode, whereby we can obtain fractions of liquid pyrolysis products with cyclopentadiene content ranging from zero to the maximum possible, which is equal to the initial content of dicyclopentadiene fraction. At low temperatures, the equilibrium of the reaction is displaced toward dicyclopentadiene, and therefore obtaining stable quality petroleum resins using polymerization of so-called redistilled (distilled) cyclopentadiene fractions (Table 2, CF1, CF2) is closely tied to the conditions under which they were prepared: distillation speed, temperature and duration of storage of the distilled fractions.

Therefore, organizing the technological process of producing oligomers of a constant and reproducible quality demands strict control over the composition of raw-materials due to the extremely high activity and constantly changing concentrations of cyclopentadiene in the composition of the fraction.

During the implementation of the industrial process used to obtain petroleum resins, the above is taken into account, and the following options are available among technological solutions:

- Removal using distillation or rectification of tar and other contaminants, and the extraction of the resulting (freshly distilled fraction) into storage until a constant concentration of cyclopentadiene is reached, without affecting the quality of the products.
- The installation of an extra column for the production of fractions with any (to the extent possible) desired ratio of cyclopentadiene and dicyclopentadiene, which will almost immediately be subjected to polymerization. This will allow one to obtain a small batch of products that are "made to order," corresponding to the interests of any customer.

Table 2
The composition of the fractions of liquid pyrolysis products [76].

Components	The composition of the pyrolysis product liquid fraction,%					
	C_9	SF	DF1	DF2	CF1	CF2
Cyclopentadiene	4.3	0.5	4.5	4.0	18.2	20.2
Benzene	3.0	1.9	5.0	6.6	5.0	6.6
Toluene	8.8	10.5	7.8	7.0	7.8	7.0
Ethylbenzene	5.7	3.8	0.7	2.4	0.7	2.4
Xylol	23.7	24.1	0.9	11.0	0.9	11.0
Styrene	16.6	17.8	1.0	2.1	1.0	2.1
Methyl-ethyl-benzene	6.8	1.0	0.0	5.1	0.0	5.1
α-Methylstyrene	3.0	2.8	1.0	5.6	1.0	5.6
Dicyclopentadiene	20.1	22.1	51.3	38.2	37.6	22.0
Indene	3.2	2.3	17.2	8.9	17.2	8.9
Indene derivatives	2.3	4.5	3.3	7.9	3.3	7.9
Diemer methylcyclopentadiene	1.7	4.2	4.8	1.2	4.8	1.2
Unidentified hydrocarbons	0.8	5.0	2.5	0.0	2.5	0.0
Including unsaturated hydrocarbons	51.2	54.2	83.1	67.9	83.1	67.9

- The organization of a correction block for the composition, based on adding the prior obtained cyclopentadiene to the stable fraction in order to achieve the desired ratio of cyclopentadiene and dicyclopentadiene.

2.2. Heavy pyrolysis resin

Heavy pyrolysis resin (HPR) boils at temperatures ranging from 190 to 360 °C. The pyrolysis resin of gaseous raw materials, generated in relatively rigid conditions (temperature 815–820 °C, exposure time 1 s), is characterized by high density (1.03–1.08 g/cm^3), high aromatic hydrocarbon content (up to 87%), and aslphaltene (up to 10%) in the samples [78]. The main components of heavy resin generated by pyrolysis of straight-run gasoline are the bicyclic, tricyclic and polycyclic aromatic hydrocarbons (51–67%), as well as resins and asphaltenes (24–39%) [45]. It can be used to obtain condensed aromatic hydrocarbons: naphthalene (hereinafter decalin and tetralin), anthracene, phenanthrene, acenaphthene, and others [79,80], styrene-indene (dark) petroleum resin [81–85], and high-quality technical carbon (soot) [86–91]. Dark petroleum resin is used as a plasticizer in blends for tires and the rubber industry, as a depressive additive in order to reduce the pour point temperature of medium and highly paraffinic oils.

Thus, increasing the volume of pyrolysis production inevitably leads to the formation of considerable amounts of various types of by-products containing more than 30% of unsaturated compounds, which makes their processing, including polymerization, very cost-effective, and points to the real possibility of obtaining a wide range of hydrocarbon resins of varying structures and characteristics, as demanded by various industries.

3. Classification of petroleum resins

Petroleum resins are thermoplastic polymers with low molecular weight, obtained by polymerization of unsaturated compounds of pyrolysis liquid products. They are classified [45] based on the component and fractional composition of the raw materials from which they are derived:

- aliphatic resins derived from fraction C$_5$, mainly consisting of the isomeric pentenes, pentadienes, cyclopentadiene;
- aromatic resin C$_9$, derived based on fraction C$_8$-C$_{10}$, predominantly of fraction C$_9$. The main fractions of unsaturated compounds are styrene, α-methyl styrene, isomeric vinyl toluenes, indene;
- copolymer resins obtained based on mixtures of fractions C$_5$ and C$_9$, or a broad fraction C$_{5-9}$ with a boiling point between 30 to 200 °C;
- dicyclopentadiene-based resins obtained from technical dicyclopentadiene, dicyclopentadiene mixtures with the above fractions, or from fractions rich in dicyclopentadiene;
- modified resins synthesized by copolymerizing fractions with one another or with vinyl monomers: maleic anhydride, unsaturated acids and their esters. Hydrogenated resins are sometimes included in this group.

A variety of resins are identified mainly by the variety included in the composition of the raw fractions. It should be noted that the possibility of expanding the assortment of petroleum resins is not associated with significant investments into fixed production assets. It is enough to vary the operating modes of current rectification and distillation equipment and upgrade the raw material selection schemes, thereby changing the composition of the raw material fractions. Furthermore, the properties of the products obtained via polymerization of unsaturated compounds derived through liquid pyrolysis, especially catalytic polymerization, are largely dependent on the preparation method of the raw materials.

The expansion of the range of raw materials of liquid pyrolysis products can be supplemented by the use of various catalysts and initiators: we can obtain different types of resin, with various physical, chemical, and technical characteristics [92–101], while still using the same type of raw material fraction. The separation and granulation of PR also has a serious effect on the physical and chemical properties (color, softening temperature, unsaturation) and consequently, on the possible use of petroleum resins in a particular industry.

The structure of resin use (%), associated with the classification of its structure [102], is as follows: C$_5$- and dicyclopentadiene resins (37.1), C$_9$- and indene-coumarone resin (44.4), hydrogenated or water-white (18.5). Naturally, this pattern of usage will change over time, but the proportions will remain largely the same.

4. The polymerization techniques of using liquid pyrolysis products

The petroleum resins that are successfully used instead of natural resources are obtained using methods of ionic (cationic) [52,53,103] and radical (thermal, initiated) polymerization [45,52,104,105].

The components of liquid pyrolysis products, containing electron-donating substituents on the double bond (styrene, α-methylstyrene, isobutene, propene, and others) can polymerize via the cationic mechanism. Diene compounds found in the raw materials (cyclopentadiene, dicyclopentadiene, isoprene, etc.) are also involved in cationic polymerization, and form unsaturated polymers. The catalysts involved are various substances, among which we find the following groups: proton acids (H_2SO_4, H_3PO_4, $HClO_4$, CF_3COOH etc.); aprotic acid – Lewis acid ($AlCl_3$, BF_3, $AlBr_3$, $SnCl_4$, $TiCl_4$, $FeCl_3$) and their complexes, as well as Ziegler–Natta catalyst systems based on halides and oxyhalides of metals having variable valence and organometallic compounds. The process is usually carried out under atmospheric or slightly positive pressure (0.1–0.2 MPa) and low temperatures (20–80 °C), in compliance with the special measures required to prevent the corrosion of equipment.

Unlike ionic processes, the radical synthesis processes for petroleum resins are carried out at high temperatures and pressures: thermal polymerization occurs at 250–280 °C and a pressure of 0.8–1.0 MPa, and initiated polymerization occurs at a slightly lower temperature of (160–220 °C) and pressure, using peroxide and other peroxy ester initiators. The production of resin using thermal methods is the most simple in terms of technology and hardware design. The flowsheet for initiated

polymerization is largely similar to that of thermal polymerization, but also contains the storage node and initiator dosing [45]. Russian industries use mainly radical processes: thermal [106–109] and initiated polymerization [110–113].

4.1. Comparative characteristics for preparing petroleum resins

A comparative evaluation of obtaining petroleum resins is given in References [45,114–117], and allows us to conclude that the yield from the raw materials is reduced according to the following order: cationic (catalytic) > thermal > initiated process, which is associated with the monomer activity present in the fractions of liquid pyrolysis products. The total monomer conversion during the thermal process is lower in comparison to the cationic, comprising 81.1 and 97.5%, respectively. The lowest conversion of unsaturated hydrocarbons takes place in the initiated process; in this case α-methylstyrene, dicyclopentadiene, indene and vinyl toluenes do not enter into the polymerization actively enough. The difference in the conversion of unsaturated hydrocarbons determines the composition of petroleum resins. For example, resins obtained via ionic polymerization are copolymers that include styrene, vinyltoluene, indene and dicyclopentadiene; styrene is the main binding link in the resin compositions synthesized using radical mechanisms [45].

Since the actual appearance of petroleum resins as a large-scale product, various researchers have attempted to analyze the advantages and disadvantages involved in the various methods of their preparation. For example, in Reference [114] we have the results of comparing the polymerization of "light oil" using AlCl$_3$ (0.5 %, 15 min) and the thermal method (220–230 °C, 0.2–0.4 MPa, 3 hrs.). These polymerization results are described as the most efficient by the authors. As a result it was concluded that the yields are slightly different (1.5–2.0%), but that the catalytic method is more suitable for obtaining high melting resins.

A comparison of the polymerization results of fractions with boiling temperatures between 130 and 190 °C is presented in Reference [117]. AlCl$_3$ was also chosen as a catalyst, but was used under other circumstances: 3% for raw materials, 60 °C, for 1 hr. The initiator process was carried out with 2% hydroperoxide from isopropyl-benzene, 120 °C, 30 hrs.; the thermal process was at 250 °C, 0.8 MPa over the course of 5 hours. A comparison of the methods was carried out using the following criteria: yield, conversion of individual monomers, softening temperature of the product and its usefulness in various industries. Unlike results from previous work, it was shown that a higher yield of resins was made using the catalytic process and, naturally, this involved the maximum conversion of monomers, which determined the product composition; the lowest output was created by initiated polymerization. However, according to indicators such as color, ash content, volatiles content, flash point, resins obtained using initiated and thermal polymerization are preferable, based on which the authors concluded that in general thermal polymerization is best.

From the comparison of technical and economic indicators pertaining to various petroleum resin production methods [45],

it follows that the most economic method of production is thermal. In this case the cost is 27% lower than when using the catalytic method. Unfortunately, based on the data submitted it is difficult to make an adequate assessment. Results of the analysis indicate that the use of a catalyst creates a higher cost for resins, by way of the cost of purchasing, transportation, warehousing, storage and preparation of the catalyst (catalyst systems), the use of metering devices, corrosion-resistant materials, neutralization (deactivation) of the catalyst system and the removal of its neutralization products (decontamination), tar recycling, drying the resin and unreacting hydrocarbons. The process of neutralization (deactivation) of the catalyst (catalyst system) is largely what determines the cost of the resins, as indicated in Reference [116], given comparable physical and chemical characteristics of resin.

The authors of Reference [115] compared the methods using the following experimental conditions: thermal process – 250 °C, 6 hrs.; initiated process – 1% of monoperoxene, 200 °C, 6 hrs.; catalytic process – complex AlCl$_3$–C$_6$H$_5$CH$_3$–H$_2$O (1:1.2:0.08; mass), complex concentration 2%, 60 °C, 2.5 hrs. Unreacted hydrocarbons were separated from the resin using atmospheric and vacuum distillation. It is shown that the resin obtained using the initiated method has a higher softening point than the resin that is thermally obtained, all other physicochemical characteristics being equal. According to the authors, the disadvantages of the thermal method include low yield, as well as the high temperature and pressure involved in the process. The disadvantages of the initiated process include low resin yield and the necessity of using fire and explosive initiators. The catalytic method allows for the achievement of maximum yield of resin and the maximum conversion of monomers, but has its disadvantages – the resins have a dark color and low unsaturation. The last indicator is considered to be a positive by many researchers, likely assuming that the resin quality indicators have a high stability during storage or when used in various formulations. The disadvantage of catalytic processes is also a multi-step process. The authors of Reference [115] conducted an analysis of the synthesis methods involved in petroleum resins and their areas of application, and do not give a categorical assessment in favor of any production method, but note the following. Regardless of the many advantages of the initiated and thermal polymerization methods, catalytic methods have distinctive features: the ability to widely vary polymerization conditions and, respectively, synthesize resins that are characterized by different softening points and color; high speed of the process; availability of low-cost catalysts; simple process and ability to create continuous technological schemes when feeding the catalyst in the form of a complex. However, the authors of Reference [115] also note that the lightest resins, which are critical for the paint industry, can be obtained using initiated polymerization. In this same article it is indicated that an important factor affecting the physical and chemical characteristics of PR, is the stage when the resin is separated from unreacted hydrocarbon, which is characterized by the use of atmospheric pressure or vacuum, while gradually increasing the temperature. The catalytic methods for the synthesis of petroleum resins are the most common outside of Russia.

From the studies mentioned above, not one of the comparative analyses is sufficiently convincing, since the conditions involved in producing petroleum resin are selected arbitrarily, and the characteristics involved in the criteria do not match. The economic calculations are not entirely justified, since the costs do not include many factors that could seriously adjust the results and opinions of the authors. All assessments of technical and economic efficiency of the methods used to obtain resin, relating to catalytic methods, are carried out using AlCl$_3$ and other complexes based on the same, and do not discuss other catalytic systems.

In analyzing the methods involved in producing petroleum resins, which use different initiators and catalysts, it should be noted that each method, together with certain benefits, also has specific disadvantages, but adjusting the process conditions can yield resins of different quality: light and refractory, with a high or low molecular weight, different degrees of brittleness and color. In our opinion, the greatest potential for development is in the catalytic process of producing petroleum resins. It can be implemented using a broad range of catalysts, technical recycling possibilities, complex agents, deactivation methods (neutralization), with the formation of organic compounds, without deteriorating the physical and chemical parameters of the resins.

5. Catalytic processes for preparing petroleum resins

Catalytic synthesis methods of petroleum resin include the following basic steps: preliminary preparation of raw materials, polymerization, neutralization of the polymerization (deactivation of the catalyst) and its washing, stripping of unreacted hydrocarbon, drying and granulation of the resin.

Protic and aprotic acids are used as catalysts.

The early stages of developing petroleum resin synthesis on the industrial scale included the mastering of a method that used H$_2$SO$_4$, which was first proposed as a method of pretreatment for liquid pyrolysis products from unsaturated compounds, in order to improve the quality of the emitted benzene [103]. This method involves using 0.5–2% H$_2$SO$_4$ (or in conjunction with AlCl$_3$) in order to polymerize the unsaturated compounds. This method was attractive because its catalyst was a liquid during storage, and dispensing it did not present any technical problems. In addition, sulfuric acid has an acceptable solubility in pyrolysis products. This method allows for the obtainment of polymer products with a yield of 30–40%, in mild conditions and using equipment that does not require high strength characteristics.

However, the use of H$_2$SO$_4$ required the utilization of corrosion-resistant materials: alloyed steel, cast iron or acid-alkali-resistant enamels. The color of the obtained resins makes them difficult to use in the production of bright paint products. Furthermore, in parallel to the main polymerization reaction, there were processes of hydrocarbon sulfation via unsaturated bonds, with the formation of alkyl (aryl) sulfonates or sulfates, whereas during catalyst neutralization the NaOH or NH$_3$ aqueous solutions formed surfactants that facilitated the formation of stable emulsions. Therefore, in order to obtain resins in commercial form, the use of demulsifiers and anti-foaming

agents was required; however, their presence is not always desirable.

Later on, petroleum resin derivation methods using protonic acids were improved. For a catalyst, the use of H$_3$PO$_4$ in a mixture of H$_2$SO$_4$ [118] or sulfonates [119,120] was proposed. Reference [121] proposed the use of the RSO$_3$H–2CH$_3$COOH system to polymerize the unsaturated hydrocarbons that did not react at the first, thermal stage of polymerization of the liquid pyrolysis products. Each method had a number of specific problems that did not allow for the study to continue beyond the laboratory or experimental setting.

The interesting variants to the analytical processes involved in obtaining petroleum resins are associated with the use of liquid HF [114]. The main disadvantage of this method is the fact that HF is highly toxic, which requires the equipment to be hermetically sealed. The formation of hydrofluoric acid, which causes increased corrosion of the equipment when it comes into contact with water, also complicates the process. The flowsheet of polymerization under the influence of gaseous HF is different from the flowsheet involving liquid catalysts, due to the fact that instead of a good cooling reactor with stirring, there is a need for a reactor-absorber set, which receives the HF gas through a bubbler. After reaching the desired degree of conversion, the polymerizer is heated, and HF is removed from the reaction mass. The remaining hydrogen fluoride is washed with an alkali solution. The amount of HF circulating in the system is 10–12% of the raw material in the reactor. During polymerization involving gaseous HF, the resins come out being lighter than those obtained using liquid HF. One advantage of this method is that it yields fewer insoluble, infusible resins and there are no emulsions.

The use of Lewis acids allowed us to simplify the technology of petroleum resin isolation. A series of studies by L.A. Potolovsky [103,122,123], discloses a method for obtaining resin using powder AlCl$_3$, which allows us to obtain a clear refractory product with a softening point of 85–90 °C. Experience in the industrial use of dry AlCl$_3$ as a polymerization catalyst of a broad fraction of liquid pyrolysis products (25–200 °C) is presented in Reference [114], which also shows the data of the material balance of productions and physio-chemical characteristics of the resulting resins. Furthermore, this method was developed by authors both domestically [124,125] and abroad [126–130]. Reference [131] shows the results of using AlCl$_3$ to polymerize fractions with boiling temperatures of 140–200 °C, produced during the pyrolysis of natural gas, gasoline, kerosene, and light gas oil. It is noted that the resin yield is maximized when gasoline is used as a raw material, and when the raw materials are ballasted, the yield is significantly reduced along with a simultaneous decrease in the molecular weight and softening temperature.

However, dry AlCl$_3$, together with benefits such as availability, low cost, high activity and low demands for the content of water and other mixtures, also has a number of disadvantages. The high absorbability and formation of lumps of the catalyst, which complicates its dosage and distribution in the reaction mass, lead to insufficiently clear repeatability of the process parameters, and actual catalyst losses. The partial deactivation

of the catalyst during hydrolysis is accompanied by the release of hydrogen chloride into the atmosphere, which considerably degrades the environment and reduces the equipment function. In addition, the absorbability of the catalyst demands the use of air or an inert gas with a high degree of dehydration during pneumotransport, which leads to additional costs. And yet, the use of $AlCl_3$ became widespread all over the world among cationic catalysts, in the synthesis of petroleum resins.

In order to eliminate the drawbacks mentioned above, liquid complexes of $AlCl_3$ that are just as active as powder $AlCl_3$ were proposed in accordance with conclusions drawn by the authors. In order to improve the solubility of $AlCl_3$ in liquid pyrolysis products, it was combined with oxygen- and halogen-containing compounds: carboxylic acid [132,133], anhydrides [134,135] and halides [136], olefin oxides [137], aromatic and aliphatic esters [138–141], monohydric [142–144] and polyhydric alcohols [143], HCl [145–147], mercaptans and amines [148,149].

The authors of Reference [150] claim that the lower alcohols have their own specific acidity, as a result of which the system $AlCl_3$–CH_3COCH_3–C_4H_9OH–H_2O is the most effective for the oligomerization of piperylene (component of fraction C_5). References [151,152], consider getting resin from fraction C_9 in the presence of complexes of $AlCl_3$–C_2H_5OH and $AlCl_3$–$C_6H_5CH_3$–H_2O. For the first set, the resin molecular weight dependence on the ratio of C_2H_5OH: $AlCl_3$ has an extreme character with a maximum at 1.5: 1, based on which we can conclude as to the inhibition of the cationic polymerization mechanism. In the second catalyst complex, it was noted that the process of temperature increase from 60 to 80 °C increases the yield of resin from 18.7 to 50.9% (for this temperature range, this is quite unusual) with a deepening of color 65 to 110 units. In [133] as a promoter to $AlCl_3$, we have a mixture of alcohols C_{1-5}, carbonyl compounds C_{1-13} and water at molar ratios (10.0–98.0): (0.9–5.2): (1.7–7.0): (1.0), respectively. R.Z. Azanov [144] chose the optimal conditions for obtaining petroleum resins from fractions C_5, C_9 under the influence of a catalyst system $AlCl_3$–acetone–water–butanol (1: 0.45: 0.1: 0.45), and proposed a three-stage process with a decimal catalyst feed, providing 84% yield of the resin (based on the fraction of the monomers) and a molecular weight of 750, softening point 85 °C, an iodine value of 52 g I $_2$/ 100 g, color 60 mg I_2/100 cm^3 KI. The oligomerization of fraction C_9 [141] in the presence of 1–2% of the catalyst system $AlCl_3$ – electron donor (Ph_2O, Bu_2O, $OC(NH_2)_2$, $MeCOOEt$, Me_2NCHO) – H_2O at 20–90 °C allows for synthetization of resins with improved color (10–60 mg I_2/100 cm^3 KI) and a molecular weight of 600–700. It is found that the reaction proceeds according to the mechanism of "live" chain formation: the process has room only for initiation and chain propagation, and chain growth has no limit.

The use of other aluminum halides in the presence of oxygen-containing promoters is proposed in References [132,142]; however these proposals go no further than lab experiments.

A significant number of publications present the results of polymerizing liquid pyrolysis product fractions in the presence

of BF_3 [153], its complexes with ethers [154–157], phenol [155,158,159], alcohols [155,158,160] amine [155,160], hydroperoxides of hydrocarbons [155] and water [161] as well as in the presence of complexes of $AlCl_3$ with BF_3 [162]. In particular, Reference [163] discusses some general patterns of polymerizing a broad fraction (25–200 °C) and fractions 25–80 °C at 40 °C under the influence of the complex $BF_3 \cdot O(C_2H_5)_2$ in the concentration range of 0.1 to 0.4% Resins with a molecular weight of 200 to 350 were obtained; the molecular weight increased with the duration of the process. Based on IR- and ^{1}H NMR- spectra, we were able to conclude that the oligomerization diene and alkenyl aromatic hydrocarbons are preferred.

Using the complex $BF_3 \cdot O(C_2H_5)_2$ in the polymerization of a fraction with a boiling range of 190–230 °C allows for the release resins (up to 65%) [157]. In this case, the fraction is heated while stirred for 1 hour at a temperature of 200 °C, and then the temperature is reduced to 60–90 °C while adding the catalyst; then the reaction mixture is stirred for 2 hours at 155 °C. The softening temperature of the obtained PR – 90 °C, the color – 85 mg I_2/100 cm^3 KI, iodine value – 34.5 g I_2/100 g.

When using the combined catalytic complex of $BF_3 \cdot O(C_2H_5)_2$–$AlCl_3$–HCl, the authors of Reference [164] derived petroleum resins with a yield of 78% and high physical-chemical indicators (the color – 20–40 mg I_2/100 cm^3 KI, the softening temperature – 75 °C). The process was carried out in two stages: the first stage involved the synthesis of petroleum resins in the presence of $BF_3 \cdot O(C_2H_5)_2$; the second was the separation by distillation $BF_3 \cdot O(C_2H_5)_2$, and adding 3% catalyst complex $AlCl_3$–HCl to an oligomer cooled to 30 °C. The total duration of oligomerization was 2.5 hours at 80 °C.

The catalytic system based on BF_3 and $AlCl_3$ was used in the preparation of the copolymer resins from a mixture of fractions of C_9 and C_5. In order to prevent the formation of polydicyclopentadiene, the process was conducted in the presence of 0.03–0.20% (by weight of the monomers) $BF_3 \cdot Et_2OH$ at 60 °C for 10–30 min. After this, 0.5–1.0% $[AlCl_3OH]^-H^+$ was added, and the process was performed under the same conditions for another 60–85 min. This method allowed to obtain bright resin (30–80 mg I_2/100 cm^3 KI) with a higher yield (37–45%) than in the case of using $BF_3 \cdot Et_2OH$ (35–40%), with less consumption. The reaction rate is thus lower than in the polymerization of each catalyst alone [162].

The results of applying $FeCl_3$ for the obtainment of resin using fractions with a boiling range 130–260 °C are given in Reference [119]. Research of polymerization under the influence of 4–10% $FeCl_3$ at 40–80 °C for 5–90 minutes has shown that the optimal conditions for obtaining resins with a yield of 25.9% and a softening point of 81 °C, are the following: 6% of catalyst 60 °C and 40 min. However, in the process of isolating the resin by washing with water we get HCl, and together with ferric hydrate we get a stable emulsion. A heterogeneous system was proposed as an alternative: $FeCl_3$ (5%) of the silica gel will eliminate the formation of emulsions with a slight decrease in resin output, down to 23.9%. The catalyst is regenerated by washing with a fresh portion of the raw material. Working with complex $FeCl_3 \cdot H_2O_2$ showed the ability to achieve resin yields of 30.6% from the fraction 130–260 °C and 27.3% – from

fractions 160–230 °C; resin softening temperature – 81.5 and 88.0 °C, respectively.

Possibility of using $SnCl_4$ has been investigated in the synthesis of resins using fraction C_5 [147], and aromatic fractions of petroleum cracking [160].

A considerable number of studies have been devoted to the use of $TiCl_4$ in the process of polymerizing petroleum cracking fractions, and liquid pyrolysis products. Chloride titanium is currently an available reagent, its use in the production of petroleum resins has industrial importance, particularly in the polymerization of fraction C_5 [147,165,166], or piperylene (piperylene fraction) [167] when obtaining varnish. In order to improve the adhesion of hydrocarbon resins, the use of Friedel–Crafts catalysts, comprised of $TiCl_4$, is proposed for processes of polymerizing petroleum cracking fractions with boiling temperatures of 140–280 °C, and the various dienophile modifications thereof [168]. Studies have found that the activity of mixed catalyst $AlCl_3$–$TiCl_4$ [169–171] is lower than the activity of $AlCl_3$, but higher than that of $TiCl_4$. When it comes to the cationic oligomerization of piperylene, titanium etherates also have low catalytic activity, which is markedly inferior to that of similar complexes $AlCl_3$ [172]. Using individual $TiCl_4$ also leads to low yields of dark-colored resin (1400–1500 mg I_2 / 100 cm^3 KI) in the case of the polymerization of fractions from liquid products of straight-run gasoline pyrolysis 130–190 °C, with different ratios of the main monomers (styrene: dicyclopentadiene) [134].

In addition to Lewis acids, the Ziegler–Natta ion coordination systems based on $TiCl_4$ and organoaluminum compounds [173] can be used as catalysts for the polymerization of liquid pyrolysis products. The organoaluminum compounds are known to be less "stiff" than those with $AlCl_3$, and allow one to work with diene hydrocarbons. The regularities of the polymerization of fraction C_5, containing a significant number of dienes (20–30%), under the influence of heterogeneous catalyst systems based on $TiCl_4$, VCl_4 (on $MgCl_2$) given the restoration of their $Al(iso\text{-}C_4H_9)_3$ in the presence of electron donors (esters, alcohols, tetrahydrofuran) and methyltrichlorosilane, at 60 °C for 2 hours (concentration of $TiCl_4$ – 0.017 mol/l) are examined [174]. Improved diene content in the reaction mass of 25%, the increase in the heat treatment temperature of the catalyst up to 120 °C, and the molar ratios of Mg/V and Ti/V being 1:3 leads to a marked acceleration of the process and a decrease in the molar mass of the resin with a molecular mass of 1500–1800, good solubility in toluene, nephras, and compatibility with vegetable oils.

Homogeneous catalyst systems were used to obtain petroleum resins from the fraction C_5 and heavy resin pyrolysis: $TiCl_4$–CH_3COOH, $TiCl_3$–$Al(iso\text{-}C_4H_9)_3$ и $TiCl_4$–$Al(iso\text{-}C_4H_9)_3$ [81,82].

Homogeneous catalytic systems based on a titanium chloride and organoaluminum compounds have found application in polymerization of unsaturated compounds of other fractions of liquid straight-run gasoline pyrolysis products. Patents [175–177] proposed using systems containing $TiCl_4$ и $Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$ and $Al(iso\text{-}C_4H_9)_3$, including production waste of $TiCl_3$ and organoaluminum compounds, in order

to synthesize PR from high-boiling fractions with boiling points between 130–190 °C. Carrying out the polymerization in a homogeneous environment allows for the precise control of process parameters, and therefore, the reception of a consistently high-quality PR [74,75,175–183]. It was shown that $TiCl_4$ and individual organoaluminum components have a low catalyst activity during polymerization, and the use of the catalyst system $TiCl_4$, which is an organoaluminum compound with a molar ratio of 1: (0.3 ÷ 1.0) supports the increase of the oligomer yield and the improvement of their properties. Also, the catalytic activity of the system has no significant dependence on the nature of the organoaluminum component and decreases according to: $Al(C_2H_5)_2Cl > Al(C_2H_5)_3 > Al(iso\text{-}C_4H_9)_3$. Unsaturated compounds of fractions of liquid pyrolysis products, such as styrene and dicyclopentadiene, are successfully polymerized under mild conditions: at a temperature of 60–80 °C, and $TiCl_4$ concentration of 1.5 to 2% over the course of 120–180 mins with the formation of 29–56 % oligomers having a molecular weight of 500–700.

After the polymerization process is complete, further contact of the catalyst with the reaction mass is undesirable, and in most cases the polymerizate must be neutralized, and the neutralization products must be removed. These stages of PR synthesis are of great importance for the quality of the obtained resins. The developed method for wasteless decontamination of catalyst systems by epoxy compounds (oxides, propylene and styrene, butyl glycidyl ether and phenyl, and epichlorohydrin epoxycyclohexane) allows us to greatly simplify the process of resin extraction with the formation of organo-soluble alkoxy derivatives of titanium and aluminum [93,184–186]. It is shown that the presence of catalyst deactivation products in the resin does not impair product specifications thereof (color, adhesion, strength at flexing and impact), and in some cases has an additional plasticizing effect.

Modifying the composition of the initial fraction typically requires changing the composition of the catalyst systems. This is especially true when you use fractions rich in dicyclopentadiene. Thus, the composition and activity of fractions containing dicyclopentadiene change during preparation by partial depolymerization of dicyclopentadiene, and cyclopentadiene content increase. In this regard, we see the urgency of using new catalysts $Ti(ORCl)_nCl_{4-n}$ or catalyst system $Ti(ORCl)_nCl_{4-n}$–$Al(C_2H_5)_2Cl$ in an equimolar ratio of the components during polymerization of cyclo- and dicyclopentadiene containing fractions, and this allows us to obtain light petroleum resins at a yield of 30–38% at 40–60 °C for 60 min [187–190]. The activity of $Ti(ORCl)_nCl_{4-n}$ depends on the degree of substitution of chlorine atoms in $TiCl_4$ and the type alkoxy substituent, and decreases according to: $Ti(OC_6H_{10}Cl)Cl_3 > Ti(OC_3H_7Cl)Cl_3 > Ti(O_2C_9H_{10}Cl)Cl_3 > Ti(OC_9H_8Cl)Cl_3$.

Thus, a catalytic process for preparing petroleum resins is very promising since it allows for widely varying properties of the resulting products, depending on the catalyst used, and provides high yields at moderate synthesis temperatures.

The complex processing circuit for liquid pyrolysis products provides a more complete and efficient use of both unsaturated

and saturated hydrocarbons. When considering the benefits of one approach to processing liquid pyrolysis products over another, researchers typically do not spend enough time on issues related to the use of components that have not entered into polymerization. Calculating a monomer conversion of 85–95%, based on their content in the initial fraction, does not show the extent of this problem. However, when considering the indicator of "yield per initial feedstock," we can conclude that the volume of petroleum resin production is close to the volume of non-polymerizable components.

The solution to this problem could be as follows: since after fraction polymerization and the isolation of resin there is always a non-polymerizable component (distillate), composed mainly of saturated hydrocarbons, it can be used as "solvent oil."

The mixture of non-polymerizable components after fraction polymerization C_5 and dicyclopentadiene separation can be returned to pyrolysis together with naphtha.

BT (Benzene-toluene) or BTX (benzene-toluene-xylene) fractions, isolated from the distillate after the polymerization of fraction C_9 or broad fraction C_{59}, can be subjected to hydrodealkylation in order to produce benzene, which is highly valuable.

The polymerization of dicyclopentadiene fractions using any catalysts leads to a low yield of the corresponding resin. Chromatographic analysis of non-polymerizable distillate components after the polymerization of this fraction (DF) [191] has shown that it is a mixture of about 80% dicyclopentadiene. Obviously, this distillate can be used successfully to obtain highly pure dicyclopentadiene, with subsequent derivation of polydicyclopentadiene. The distillate can also be used for partial or complete monomerization of dicyclopentadiene, and further use of the products obtained: the cyclopentadiene or the cyclopentadiene-dicyclopentadiene mixture, respectively [192].

Thus, the non-polymerized components, after the polymerization of different fractions of liquid pyrolysis products, can be isolated and used as commercial goods or as initial raw materials in the production of individual compounds, which allows us to solve the problem of resource conservation by way of complex processing of pyrolysis by-products.

6. Conclusions

The basic process for producing lower olefins (ethylene, propylene) at present is high temperature pyrolysis of various types of hydrocarbons, accompanied by the formation of considerable amounts of by-product liquid.

Liquid products of pyrolysis ethylene-propylene units (pyrolysis fractions), containing a significant amount of unsaturated hydrocarbons, are the raw materials for petroleum resins. Varying the composition of the initial fractions of liquid pyrolysis products can significantly change the properties of the resin, thereby expanding their range and scope.

Petroleum resin can be obtained by radical and ionic (cationic catalyst) polymerization. At present there is no unambiguous understanding of which of the methods used to obtain petroleum resins is the best, and has the maximum benefits. The simplicity and versatility of the technological design of the thermal and initiated processes (radical polymerization) also create limitations on resin characteristics and, accordingly, limit their range and applications. The high temperatures and pressures used in radical polymerization also create further restrictions in the selection and arrangement of the equipment.

Catalytic methods (ion polymerization) are more promising when it comes to producing petroleum resins, because they allow us to conduct the process at a faster rate and under milder conditions, while achieving maximum yield (maximum conversion of monomers), which is the determining factor in resource conservation. The developed methods of deactivation (neutralization) catalyst systems, with the formation of organo-soluble compounds that do not impair the physical and chemical indicators of the resin, eliminate any deficiencies in the ionic process. When it comes to ionic polymerization catalysts, there is considerable interest in Ziegler–Natta catalyst systems, which are based on organometallic compounds and transition metal halides, which allow us to conduct the process in a homogeneous environment, accurately control the process parameters, and consequently, obtain high quality products.

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