
REVIEWS

Production of High-Density Jet and Diesel Fuels by Hydrogenation of Highly Aromatic Fractions (Review)

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Abstract—Physicochemical characteristics and hydrocarbon composition of highly aromatic wastes (light gas oil from catalytic cracking, pyrolysis tar, coal tar, coal gasification tar) as a feedstock for producing high-density jet fuels are considered. The hydrogenation reactions of polycyclic aromatic hydrocarbons, including mixtures of hydrocarbons with different numbers of rings, are described. Catalysts for hydrogenation of highly aromatic waste to obtain fuel fractions are considered. Particular attention is paid to catalyst deactivation in the course of processing of this feedstock. A separate section deals with the choice and implementation of procedures for processing highly aromatic feedstock to obtain jet and diesel fuels.

Keywords: high-density jet fuel, pyrolysis tar, coal tar, high-energy fuel

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INTRODUCTION

Production of specialty high-density aviation fuels with high volumetric heat of combustion and high thermal oxidation stability is a strategic problem extremely important for the development of unmanned and military aviation. The thermal oxidation stability is one of the main characteristics of fuels intended for supersonic aircrafts, because the fuel is used for cooling the aircraft structural parts that are subjected to kinetic heating from friction with the high-velocity ram air flow. In addition, improvement of aviation gas turbine engines is accompanied by elevation of the air and gas temperature along the engine tract, i.e., by an increase in the heat stress and, as a consequence, by an increase in the heat transfer to the fuel [1]. For example, at a flight velocity of 3M, the fuel can undergo heat-up to 350°C and higher temperatures, which will inevitably cause thermal degradation of paraffin hydrocarbons and accelerate coking and dehydrogenation [2]. Along with enhancing the thermal oxidation stability of jet fuels for supersonic aircrafts, studies are being

performed to develop endothermic fuels ensuring additional heat pick-up via endothermic reactions, e.g., dehydrogenation [2]. The most important properties of aviation fuels, influencing the prospects for their use, are the heat of combustion and density, determining the fuel consumption, possible fuel amount that can be taken on board, and, as a consequence, the flight range.

Heat-resistant T-6 fuel developed in Russia in the second half of the XX century contains 75–80% naphthene hydrocarbons and has satisfactory energy parameters [3]. It is produced in small amounts by deep hydrogenation of a mixture of gas oil from coking of petroleum residues and light gas oil from high-pressure catalytic cracking [4]. Therefore, all the training flights on supersonic planes are performed using RT fuel, which decreases the flight range [1]. In the United States, military aviation uses JP-7 and JP-8 hydrocarbon petroleum fuels with enhanced thermal oxidation stability, and a process for production of JP-900 high-density heat-resistant jet fuel from coal gasification and coking tars and light catalytic cracking gas oil has been developed [3]. Hydrogenation of highly aromatic coal-derived frac-

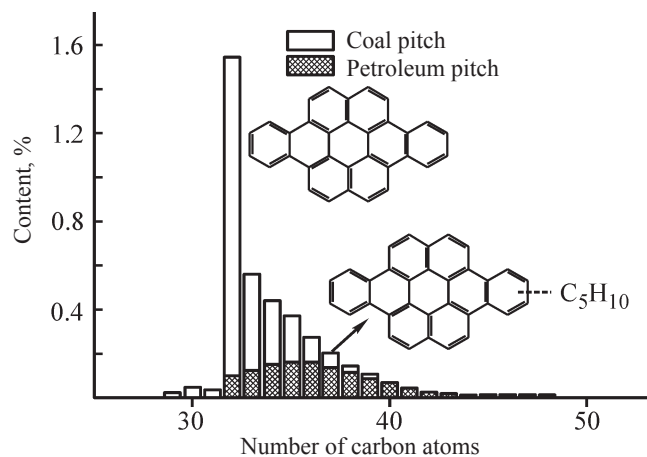


Fig. 1. Distribution of hydrocarbons with DBE = 25 from coal and petroleum pitch with respect to the number of carbon atoms [10].

tions allows production of fuels containing up to 90% naphthene hydrocarbons and no n-alkanes, which ensures high density, high thermal oxidation stability, and excellent low-temperature properties, although the heat of combustion somewhat decreases [2].

Studies concerning production of alternative fuels, including jet fuels, are being actively performed in the world. Such fuels include fatty acid esters, synthetic hydrocarbons produced in the Fischer–Tropsch process, products of hydroconversion of oil-and-fat and other renewable raw materials, and products of hydrogenation of coal liquefaction and coking distillates [5]. Specifically naphthene fuels produced from aromatic hydrocarbon concentrates, including tars from pyrolysis of gasolines and light hydrocarbons and from coal coking and pyrolysis, exhibit the set of properties meeting the requirements to high-density jet fuels, in contrast to synthetic hydrocarbons produced by indirect coal liquefaction (ICL) via Fischer–Tropsch synthesis [6, 7].

Extensive studies were performed on this subject in Russia at the Institute of Fossil Fuels [8], and a process for producing motor fuels by brown coal liquefaction was suggested [9]. The fuel corresponded to the standard for RT fuel in all the characteristics. However, although the process is promising, it was not developed further, probably because of the low fuel yield based on liquid products of coal hydrogenation (9.5%), lack of industrial experience of coal liquefaction in Russia, and large expenditures. The fuel obtained has no advantages

even over common aviation kerosenes. For example, the fuel density was only 785 kg m^{-3} , and the lower heat of combustion was 43290 kJ kg^{-1} ; i.e., the volumetric heat of combustion of the fuel was 33983 kJ L^{-1} (to compare, for Naftil it is 35797, and for T-6, 36290 kJ L^{-1} [3]).

Here we summarize the data on the composition of highly aromatic wastes of different origin and on the chemistry, catalysts, and process principles of their hydroprocessing to obtain jet and diesel fuels.

GENERAL CHARACTERISTICS OF HIGHLY AROMATIC WASTES AND THEIR POTENTIAL AS A FEEDSTOCK FOR PRODUCING SPECIALTY FUELS

Highly aromatic wastes from petrochemical and coal-chemical processes include tars from coal coking, gasification, and pyrolysis, distillates from hydrogenation liquefaction of coals, tars from pyrolysis of gaseous and liquid hydrocarbons, and gas oils from coking and catalytic cracking. Despite high content of aromatic hydrocarbons as a common feature of the above wastes, they differ significantly in the fractional and hydrocarbon composition and in the content of asphaltenes and of unsaturated and heteroatomic compounds (sulfur compounds, organic acids, phenols, nitrogen bases). Before analyzing wastes from coke chemistry, essential differences in the composition of coal and petroleum distillates and residues should be noted. As demonstrated by the example of coal and petroleum pitches [10], the former is characterized by higher unsaturation (double bond equivalents, DBE) and considerably smaller number and length of alkyl substituents. The major fraction of hydrocarbons in coal pitch do not contain alkyl chains or contain short chains (less than 5 carbon atoms). This is clearly seen from the distribution of hydrocarbons with DBE = 25 with respect to the number of carbon atoms (Fig. 1). The major components of coal pitch are unsubstituted (“bare”) aromatic hydrocarbons, whereas in petroleum pitch alkyl-substituted compounds prevail. The composition of heteroatomic compounds in these two kinds of pitch is also essentially different [11].

Detailed information on the composition of hydrocarbons and heteroatomic compounds in petroleum and coke-chemical fractions and residues was gained owing to the development of such methods for studying complex mixtures as two-dimensional

Table 1. Fractional composition of coal tar [28, 32]

Fraction	Boiling limits, °C	Yield based on tar, wt %	Content of phenols, wt %	Content of bases, wt %
Light	S.B.–170	0.6	0.5	0.8
Phenolic	170–210	2.5	38.0	6.2
Naphthalene	210–230	10.0	6.0	3.8
Absorption	230–300	9.5	1.5	4.5
Antracene	300–440	25.4	0.7	6.7
Pitch	>360	52.0	–	–

gas chromatography (GC × GC) [12–14], GC × GC/MS [15–19], photoionization mass spectrometry using synchrotron vacuum UV radiation (SVUV-PIMS) [20], Fourier transform ion-cyclotron resonance mass spectrometry (FT-ICR/MS) [21, 22], and NMR spectroscopy [18]. The molecular-mass distribution of heavy fractions and residues is analyzed by size-exclusion chromatography (SEC), laser desorption mass spectrometry (LDMS), and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry [23, 24]. The use of two-dimensional gas chromatography with a mass-selective detector, of GC × LC (volatility × aromaticity/polarity), or of LC × GC × GC (aromaticity × polarity × volatility) ensures highly selective separation of groups of hydrocarbons, e.g., of polycyclic naphthene and polycyclic aromatic hydrocarbons, which is impossible when using GC × GC with separation with respect to the boiling points only [13]. Similarly, the GC/MS method in analysis of mixtures of polycyclic aromatic hydrocarbons (PCA) does not ensure accurate quantitative analysis because of incorrectness of the peak assignment. For example, problems arise in differentiation of peaks of PCA and polycyclic sulfur-containing compounds. These problems can be solved by using the GC × GC/MS method with a chemiluminescence or photometric detector [16].

On the whole, the main goals of GC × GC/MS analysis of hydrocarbon systems are detecting separate compounds, e.g., strong catalytic poisons; constructing homologous series of compounds (e.g., benzothiophenes) and revealing changes in the homologous series in the course of feedstock transformations; picking out separate conventional classes of compounds, e.g., $C_cH_hN_1S_4$, and comparing various kinds of raw materials in this respect with the aim of optimizing the process operations. The

main highly aromatic by-products showing promise as hydrogenation feedstocks are briefly characterized below.

Coal coking processes are subdivided with respect to the temperature into semicoking, or low-temperature coking (up to 500–600°C), medium-temperature coking (up to 750°C), and high-temperature coking (up to 1000°C) [25–28]. The tar yield is 4–6% in high-temperature coking and up to 18% in low-temperature coking. Semocoking tars are characterized by the highest content of oxygen-containing compounds, whereas pyridines and quinolines appear in the tar only at temperatures higher than 600°C. Semicoking tar (also termed primary tar) contains phenols, ketones, carboxylic acids, organic sulfur compounds, and aliphatic hydrocarbons, whereas the high-temperature tar (termed coal tar) consists to 95% of polycyclic aromatic hydrocarbons. The primary tar is characterized by lower fractional composition (content of the >360°C residue about 30 wt %) and lower density (900–1065 kg m⁻³). The high-temperature tar has a density of 1110–1190 kg m⁻³ and contains more than 50 wt % >360°C residue [28, 29].

The following fractions are obtained by distillation of coking tar [28–32]: light, phenol, naphthalene, absorption, and anthracene fractions and the residue (pitch) (Table 1). Tar fractions have unique composition determined by high content of polycyclic aromatic hydrocarbons, which cannot be produced from crude oil or gas.

The tar can be separated into the following fractions by liquid adsorption chromatography: paraffin–naphthene, aromatic, ether/ester, polar, and asphaltene fractions [33]. The first fraction contains mainly *n*-alkanes and alkenes up to C₂₂. The second fraction

Table 2. Content of main groups of compounds in coal tar, according to GC/MS data [33]

Group of compounds	Compound	Content, %
Paraffin–naphthene	Alkanes	10.0
	Alkenes	7.3
Aromatic	Benzene and its alkyl homologs	8.0
	Naphthalene and its alkyl homologs	10.7
	Phenanthrene, anthracene, and their alkyl homologs	7.0
	Indene and its alkyl homologs	0.8
	Fluorene and its alkyl homologs	0.5
	Pyrene and its alkyl homologs	0.5
Oxygen-containing	Alcohols	0.8
	Phenols	8.5
	Aldehydes, ketones	1.6
	Acids, ethers, esters	2.8
	Furans and pyrans	0.8
Nitrogen-containing	Pyridines	1.0
	Indoles	0.4
	Quinolines	1.0
	Anilines	0.5
	Nitriles	0.4
	Phenazines	0.1
	Carbazoles	0.9
Sulfur-containing	Thiophenes	0.01

contains aromatic hydrocarbons, of which the major components are naphthalene, methylnaphthalenes, biphenyl, anthracenes, phenanthrenes, fluoranthene, naphthacene, triphenylene, etc. The ether/ester fraction contains ketones, ethers, esters, and acridine, and the polar fraction contains phenols and quinolines. The composition of coal tar produced at the coke-chemical plant of Wuhan Iron and Steel (Group) Corp. (China) is given in Table 2. As can be seen, the tar contains 8.5% phenols, which distinguishes it from semicoking tar characterized by considerably higher content of phenols (27% in [34]).

On the whole, phenol, cresols, and ethylphenols are the most typical representatives of phenol compounds

of coking tar [35]. The tars obtained by coking of coals with a low degree of metamorphism and high fraction of oxygen-containing functional groups have high content of phenols, acids, and neutral oxygen-containing compounds [28, 36]. Compounds containing two oxygen atoms and 22–32 carbon atoms, identified as carboxylic acids, prevail in brown coal coking tar [36]. The O₄ compounds with 26 and 28 carbon atoms were identified as dicarboxylic acids, and the O₅ and O₆ compounds with DBE = 12, as anthracenes containing phenol and carboxy groups. As already noted, an increase in the coking temperature leads to a decrease in the fraction of oxygen-containing compounds in the tar [28, 36, 37]. The content of phenols passes through a maximum at

400–550°C. The concentration of guaiacols, on the contrary, decreases throughout the interval of coking temperatures (400–700°C) owing to decomposition of the methoxy group.

In contrast to [36], Shi et al. [38], when analyzing the tar from low-temperature coal coking, found no carboxylic acids among O₂ compounds; all the compounds of this group were identified as phenols on the basis of DBE. The O₂ and O₃ compounds are the most abundant according to [36], and the O₁ and O₆ compounds with DBE = 2 and 3, respectively, identified as ketenes and furans, prevail according to [39].

The most abundant sulfur-containing compounds of coal tars are dibenzothiophenes, benzonaphthothiophenes, phenanthrothiophenes, and other highly condensed structures [40]. Compounds with DBE 22–35 are the most abundant in the C_cH_hS₁ series, and compounds with DBE = 10–25 prevail in the other series under consideration. The structural similarity of sulfur-containing heterocycles and PCAs of coal tars is noted in [41]. Compounds of the general formula C_cH_hO_oS_s with *s* = 1 and 2, *c* = 15–45, and DBE up to 50 are present in large amounts. Nonaromatic compounds C_cH_hO_oS₁ with *o* = 3 and 4 and DBE = 0 were also detected [21]. The GC × GC/MS method ensures highly selective separation of alkyl homologs of benzothiophenes and of isomers with equal number of carbon atoms in the chains [42].

It should be noted that sulfur-containing compounds, as a rule, are not the most abundant class of heteroatomic compounds of coking tars, in contrast to nitrogen-containing compounds. The most abundant are compounds of the series C_cH_hO_oN_n, C_cH_hN_n, and C_cH_hN_nS_s. Among compounds C_cH_hO_oN_n, the compounds C_cH_hO₁N₄ are the most abundant, and among them the compounds with DBE < 3 prevail. That is, these compounds can be aliphatic amines. Among compounds with five nitrogen atoms, the most abundant are those with DBE = 3–4 (azoles, anilines, pyridines). The series C_cH_hON₄ mainly consists of amines and amides (DBE < 4) [39]. The above data on the prevalence of aliphatic nitrogen compounds in coal tar refer to a specific sample; for other samples, the distribution of nitrogen-containing compounds can be different [43].

Owing to unique composition, it is apparently promising to process the naphthalene and anthracene fractions by hydrogenation and hydrocracking to obtain naphthene components of fuels corresponding to jet and diesel fuels in the fractional composition. Along with

the production of fuels, coal tar is also of interest as a feedstock for the production of naphthene oils [44] consisting of polycyclic naphthene hydrocarbons with short alkyl substituents. In the tribological characteristics, such oils surpass poly- α -olefin and petroleum naphthene oils.

At high heating rate and shorter coking time, the coke yield decreases and the tar yield increases owing to exclusion of secondary cracking of liquid products [28]. Such conditions are realized when the pyrolysis is performed in reactors with a fluidized bed of coal particles. In the COED (Char Oil Energy Development Process) fluidized-bed pyrolysis process (FMC Corp.), the tar yield reaches 20% [45, 46]. The coal pyrolysis tar is, on the whole, similar in the composition to coking tars and therefore will not be considered separately.

The coal gasification yields 3–7% tar boiling in the range 120–470°C; its density is about 1030 kg m⁻³ [47, 48]. The tar produced by lignite gasification at the Lurgi plant [49–51] contains 4.37% O, 0.33% S, 0.67% N, and 0.03% ash; the H/C atomic ratio is 1.27, and the Conradson carbon residue is 3.5 wt %. With an increase in the boiling temperature of the tar fraction, the H/C fraction decreases; the O/C ratio is maximal for the 180–200°C fraction. The sulfur content tends to decrease with increasing boiling temperature: The 100–160°C fraction is characterized by higher sulfur content (0.7–0.8%) compared to the 300–400°C fraction (about 0.4%). The nitrogen content tends to increase with increasing boiling temperature.

The two-dimensional total ion current chromatogram of the gasification tar from one of the UK plants is given in the Appendix, Fig. A1 [52]. Aromatic hydrocarbons contain 1–4 rings, either unsubstituted or containing short alkyl chains. Benzene, toluene, and naphthalenes prevail. The most abundant phenol compounds are alkylphenols; indanols and naphthols are also present. Alkanes C₅–C₃₀ are present in a relatively high concentration. The tar was separated into base, acid, and neutral fractions, which were analyzed by FT-ICR MS [49–51]. This allowed construction of the series of heteroatomic compounds and hydrocarbons present in the tar, evaluation of the distribution of the tar components with respect to the number of carbon atoms and DBE (including fractions with different boiling temperatures), and determination of the most abundant series of compounds in separate fractions and in the tar as a whole.

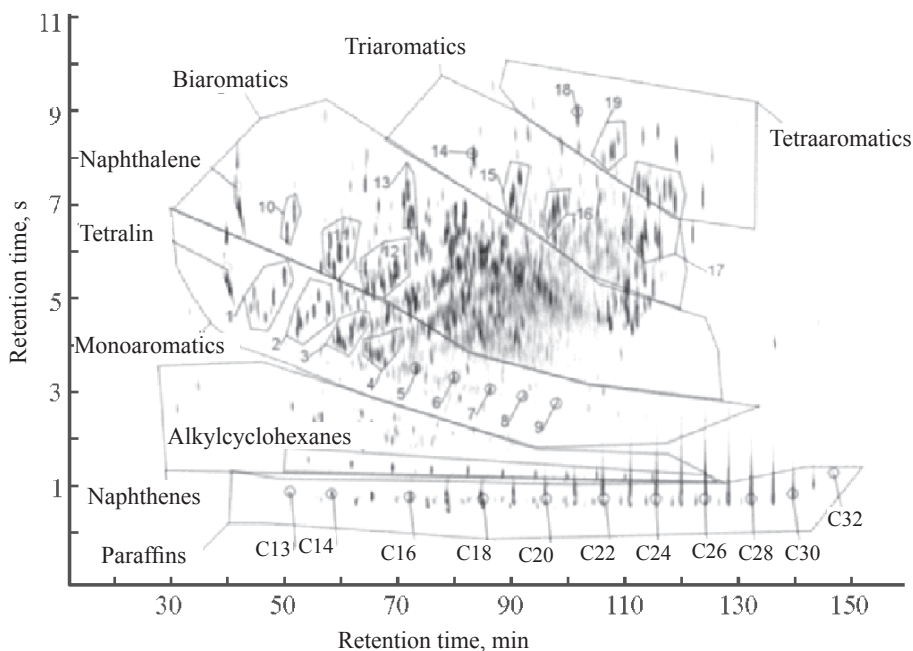


Fig. 2. Two-dimensional mass chromatogram of the 215–343°C fraction of the coal liquefaction distillate [64]. (1–9) C_1 – C_9 -Alkyltetralins, (10–12) C_1 – C_3 -alkylnaphthalenes, (13) biphenyl, (14–16) C_0 – C_2 -alkylphenanthrenes, (17) binaphthalene and its hydrogenated derivatives, (18) pyrene, and (19) C_1 -alkylpyrene.

The base fraction constitutes 2.7% of the tar, i.e., is appreciably more abundant compared to crude oil (~1%). This fraction contains phenylpyridines, quinolines, azapyrenes, dibenzoquinolines, and benzonaphthoquinolines. For compounds $C_cH_hN_1$, components with DBE = 6–9 and 12 (azapyrenes) are the most abundant.

The neutral fraction contains 16.4% paraffin-naphthene, 13.8% monoaromatic, 15.6% bicyclic aromatic, 12.6% tricyclic aromatic, and 3.4% tetracyclic aromatic hydrocarbons, 1.7% benzo- and dibenzothiophenes, and neutral nitrogen-containing compounds (indoles, carbazoles, benzocarbazoles, and nitriles). Neutral oxygen-containing compounds include ketones, phenyl ketones, acetophenones, and indanols.

The acid fraction (25.5% based on the tar) contains phenol compounds, of which the compounds with two and one oxygen atoms are the most abundant. Figure A2 in the appendix shows the distribution of compounds C_cH_hO и $C_cH_hO_2$ with respect to DBE and number of carbon atoms. The maximum in the DBE distribution for C_cH_hO corresponds to DBE = 9–16; i.e., the compounds contain 3–5 aromatic rings. The number of rings in phenol molecules does not exceed 6. Among compounds with two oxygen atoms, fatty acids prevail,

and hydroxydibenzofurans are present in a smaller amount.

Hydrogenation liquefaction of coal [H-Coal (Hydrocarbon Technologies Inc., HTI), Exxon Donor Solvent Process (EDS), Liquid Solvent Extraction (British Coal Corporation), SRC-II (Gulf Oil), etc.] [7, 45, 46, 54–56] yields mainly about 50% liquid product, including 18% fraction boiling up to 200°C and 29% fraction boiling in the range 200–520°C; the remainder is pitch. Medium-temperature distillates from pyrolysis and liquefaction of coal were considered in the United States in 1970–1990 as a feedstock for producing thermally stable jet fuel [57].

The elemental composition of the liquefaction product depends on the elemental composition of coal, number of process steps, use of a catalyst, etc. As a rule, liquefaction distillates contain up to 0.4% sulfur, from 0.8 to 3.8% oxygen, and up to 0.85% nitrogen; they have the H/C atomic ratio from 1.47 to 1.76; the Conradson carbon residue does not exceed 0.7%, and the asphaltene content, 0.4% [58–60]. The sulfur content increases with an increase in the boiling temperature of the fraction, whereas the concentration of oxygen-containing compounds is maximal in the 170–220°C fraction (4% for the H-Coal fraction [60]), which is also

characteristic for coal gasification tar [51]. The nitrogen content increases with the boiling temperature and is maximal in the residue (1.8% for H-coal), which is characteristic for all the coal-derived products [57, 60]. Oxygen-containing compounds are mainly concentrated in the distillate; compounds containing 19–24 carbon atoms with DBE = 9–13 prevail [61]. In the residue, there are oxygen-containing compounds with 18 to 44 carbon atoms and DBE distribution with maxima at 3 and 13–21.

The distribution of nitrogen-containing compounds depends on the configuration of the liquefaction process, in particular, on the use of a catalyst. Up to 50% of nitrogen-containing compounds in the distillate prepared by catalytic liquefaction of coal (H-coal) are anilines; they are formed by hydrogenation of azaarenes. Quinolines, on the contrary, prevail (~40%) in thermal liquefaction products (SRC-I) along with indolines, tetrahydroquinolines (~30% in total), and tetrahydrobenzoquinolines [62].

Distillates from hydrogenation liquefaction of coal differ from other coal-derived distillates in higher content of naphthene and naphthenoaromatic hydrocarbons. In particular, SRC-II distillate contains ~8% paraffins, ~25% naphthene and naphthenoaromatic hydrocarbons, and ~40% aromatic hydrocarbons (the remainder consists of polar compounds) [63]. The gas oil fractions contain large amounts of naphthalenes with 1–3 carbon atoms in alkyl substituents, tetralins with 1–9 carbon atoms in side chains with the prevalence of C₁–C₅-tetralins, and also phenanthrene and its C₁–C₃-alkyl homologs (Fig. 2) [64]. Alkylcyclohexanes, biphenyls, and C₁₃–C₃₂ n-alkanes are also present. Among oxygen compounds, phenols prevail (78% of all oxygen-containing compounds), with alcohols and ketones present in a considerably smaller amount [19].

Highly aromatic wastes originating from sources other than coal mainly include light and heavy gas oil from catalytic cracking and coking, and also pyrolysis tar produced at ethylene plants. Light gas oil from catalytic cracking (LGCC) has a density of 900–940 kg m⁻³ and contains up to 1.8% sulfur [65], 20–30% bicyclic aromatic hydrocarbons, about 7% tetralins, 19–35% alkylbenzenes, up to 5% polycyclic aromatic hydrocarbons, and no more than 35% paraffin–naphthene hydrocarbons [65–68]; it is also widely considered as a feedstock for producing jet and diesel fuels [69]. The content of aromatic hydrocarbons in

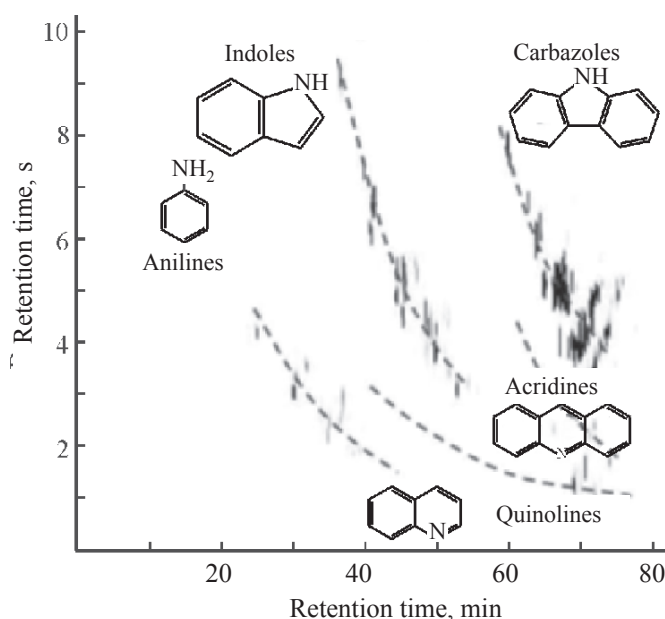


Fig. 3. Two-dimensional chromatogram of LGCC nitrogen-containing compounds [11].

the feedstock for hydroprocessing can be increased to 90–97% by LGCC extraction with polar solvents (acetonitrile, furfural) [70]. In contrast to coal-derived distillates, catalytic cracking gas oils contain in larger amounts alkyl-substituted, and not unsubstituted, aromatic hydrocarbons, which determines the largely unique properties of fuels produced from them.

LGCC is characterized by lower nitrogen content compared to coal distillates (~0.07%) and by considerably lower fraction of basic nitrogen compounds [11], which is associated with their transformation on the cracking catalyst. The major representatives of nitrogen-containing compounds in LGCC are highly condensed heterocycles: carbazoles, quinolines, and indoles (Fig. 3), which distinguishes LGCC from the straight-run diesel fraction. LGCC, in contrast to coal liquefaction distillates, contains no anilines and hydrogenated quinoline and benzoquinoline derivatives.

Among sulfur-containing compounds in LGCC, benzo- and dibenzothiophenes make up more than 80%; tricyclic aromatic sulfur compounds, ~5%; and thiophenes and sulfides in total, no more than 15% [67, 71, 72]. To compare, sulfides, thiophenes, and disulfides make up more than a half of sulfur-containing compounds in straight-run fractions. Figure A3 in the Appendix shows a 2D chromatogram of a mixture of light and heavy gas oils from catalytic cracking, recorded using a chemiluminescence detector for sulfur.

Table 3. Composition (%) of heavy tar from pyrolysis of gaseous hydrocarbons and straight-run naphtha [75]

Hydrocarbons	Pyrolysis of gaseous feedstock	Pyrolysis of naphtha
Naphthalene	11–13	9–11
1- and 2-methylnaphthalenes	6–7	5–6
Dimethylnaphthalenes	3.5–4.5	4–5
Other alkylnaphthalenes	4–4.5	2–4
Biphenyl	1.7–2.4	1.5–1.7
Methylbiphenyl	1–1.2	1.1–1.5
Acenaphthene	1.6–2	0.5–1.5
Fluorene	2–3	0.8–1.8
Phenanthrene	3–5	2–4.5
Anthracene	3.5–4.5	1–3.4

Among sulfur-containing compounds in LGCC, C_1 – C_5 -benzothiophenes prevail (more than 50% of all sulfur-containing compounds), whereas in straight-run diesel fractions their content does not exceed 20%. LGCC can contain up to 35% C_1 – C_4 -dibenzothiophenes, whereas their content in the straight-run fraction usually does not exceed 5% [71]. On the whole, catalytic cracking gas oils are similar in the composition of sulfur-containing compounds to coal tar [41] with the only difference that the coal tar also contains tetra- and pentacyclic heterocycles and also compounds containing several heteroatoms (S, N, O), absent in LGCC.

The gas oil fractions from coking are similar to LGCC to the composition of hydrocarbons and heteroatomic compounds. This feedstock contains up to 1.5% sulfur, mainly in the form of benzo- and dibenzothiophenes. Alkyldibenzothiophenes are mainly present in the fraction with the end of boiling at 375°C and higher temperatures, whereas alkylbenzothiophenes and unsubstituted dibenzothiophene prevail in low-boiling fractions [73]. The nitrogen content does not exceed 0.5%; the major nitrogen-containing compounds belong to the $C_cH_hN_1$ and $C_cH_hN_2$ series and include quinolines, benzoquinolines, pyridines with alkyl substituents, azacarbazoles, and azabenzquinolines [74]. In contrast to LGCC, the ratio of basic to neutral nitrogen compounds is high, which is due to the fact that the coking was performed without an acid catalyst. Compounds with DBE = 6–11 and 20–27 carbon atoms prevail among compounds $C_cH_hN_1$, and compounds

with DBE = 10–13 and 20–25 carbon atoms prevail among compounds $C_cH_hN_2$. The most frequent number of rings in the molecules is 3–4.

Pyrolysis of liquid and gaseous hydrocarbons gives liquid products whose yield depends on the feedstock and amounts to 2–3, 7–10, 8–12, 25–30, and 37–39% in pyrolysis of ethane, propane, butane, gasoline, and crude oil, respectively [29, 75, 76]. Heavy pyrolysis tar is present in liquid pyrolysis products in an amount of approximately 20%. It has a density of 1040–1080 kg m⁻³ and contains, along with bi- and polycyclic aromatic hydrocarbons, also aromatic hydrocarbons with double bonds in alkyl substituents: up to 5% indene, 2–3% styrene, and methylindenes [77]. The composition of heavy tar from pyrolysis of gaseous hydrocarbons and straight-run naphtha is given in Table 3 [75].

Heteroatomic compounds and hydrocarbons of pyrolysis tars are insufficiently studied compared to other highly aromatic distillates derived from petroleum and coal. Nevertheless, pyrolysis tars are attractive as a feedstock for producing naphthene fuels and polymer materials; therefore, it is appropriate to study this feedstock by gas chromatography–mass spectrometry to optimize possible processing pathways.

The other highly aromatic wastes suggested as a feedstock for producing high-density aviation fuels include residues from catalytic reforming a [78–81], in particular, residues from production of xylenes, containing about 65% monocyclic, 30% bicyclic, and 2% tricyclic aromatic hydrocarbons. An important

advantage of this feedstock is the absence of sulfur- and nitrogen-containing compounds.

The qualified approach to reprocessing of highly aromatic wastes requires detailed study of their composition and optimization of the feedstock for the corresponding processes. For example, it is important to determine the mutual influence of various aromatic hydrocarbons (alkylaromatic, bi-, tri-, and polycyclic) on hydrogenation of the mixture and on the characteristics of the fuels obtained. It is interesting to study the hydrogenation rates of the above-indicated groups of aromatic hydrocarbons and of heteroatomic compounds of various classes, present in the feedstock, and also the selectivity of transformation into complete hydrogenation products. In addition, it is extremely important to reveal the effect of various hydrogenated hydrocarbon derivatives on the operation characteristics of fuels, primarily on their resistance to heat and thermal oxidation.

CHEMISTRY OF HYDROGENATION OF POLYCYCLIC AROMATIC HYDROCARBONS

The thermodynamics and kinetic relationships of hydrogenation of aromatic hydrocarbons have been extensively studied and described in a series of books and reviews [82–84]. Here we pay the major attention to the relationships of hydrogenation and hydrocracking of various polycyclic aromatic hydrocarbons, including the cases when they are present in the feedstock simultaneously.

Hydrogenation of aromatic hydrocarbons is exothermic, and the equilibrium is shifted toward product formation by increasing the pressure and decreasing the temperature. Hydrogenation of bi- and polycyclic hydrocarbons occurs via successive reversible steps. The rate constant of hydrogenation of the first aromatic ring is, as a rule, higher; however, from the viewpoint of thermodynamics this reaction is less preferable, because the amount of hydrogen participating in it is smaller compared to the hydrogenation of the subsequent rings (1 or 2 mol of hydrogen for hydrogenation of the first ring and 3 mol for hydrogenation of the last ring) [83]. Hydrogenation can be accompanied by hydrocracking, skeletal isomerization of six-membered rings into five-membered rings, and migration of alkyl substituents. Only naphthene rings undergo hydrocracking and

skeletal isomerization; in other words; the hydrocracking rate increases with an increase in the content of hydrogenated derivatives in the reaction mixture [85].

The degree of desulfurization and hydrogenation of the substrate increases with the hydrogen pressure [86–89]. Because of thermodynamic restrictions, the temperature dependences of the conversion to hydrogenation products pass through a maximum [80, 87]. At temperatures higher than 420°C, the role of hydrocracking reactions increases; in processing of feedstock of broad fractional composition, the content of medium-temperature distillates decreases [88]. On the other hand, the degree of desulfurization and deoxygenation increases.

An increase in the feed space velocity leads to a decrease in the contact time of each molecule with the catalyst, which negatively affects the conversion to the hydrogenation products [89]. As noted in [90], the two-step hydrofining of highly aromatic distillates is a good alternative to the one-step process. In the two-step process, the first step involves preliminary hydrotreating of the feed to reduce the content of sulfur- and nitrogen-containing compounds with partial hydrogenation of aromatic compounds, and more exhaustive desulfurization and hydrodearomatization are reached in the second step. In the two-step process, high conversion of aromatic hydrocarbons is reached under milder conditions [91, 92]. In particular, the temperature can be decreased, and the feed space velocity can be increased by a factor of more than 2, which makes the technology more attractive economically.

Hydrogenation of polycyclic aromatic hydrocarbons (PCAs) is characterized by the following relationships [84]: The reactivity increases with an increase in the number of aromatic rings in the molecule; at equal number of the rings, the presence of alkyl substituents and naphthene rings favors higher reactivity; when a naphthenoaromatic hydrocarbon contains one or two rings in the molecule, external rings are hydrogenated more readily than internal rings. With an increase in the number of rings in the molecule, the conjugation energy per ring (i.e., “aromaticity”) decreases, and the bond order increases [93]. The ring with the lowest aromaticity and, correspondingly, with the highest bond order is hydrogenated first [84]. For example, the internal ring of anthracene has the lowest conjugation energy and behaves in reactions similarly to a double bond; hence, it is hydrogenated more readily than the

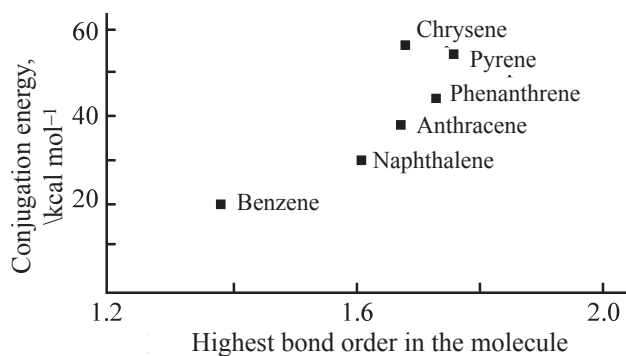


Fig. 4. Bond order and conjugation energy in molecules of some aromatic hydrocarbons [93].

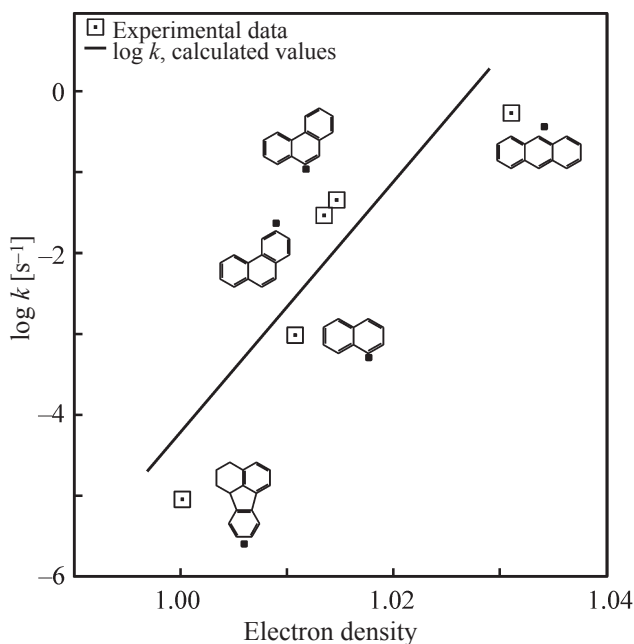


Fig. 5. Correlation of the π -electron density with the kinetics of saturation of aromatic hydrocarbons.

external rings [83]. The bond order is the highest in tri- and tetracyclic hydrocarbons (≥ 1.7), and their external rings have the bond order close to that in hydrocarbons containing two fused ring (Fig. 4) [93]. To compare, the bond order in the benzene molecule is 1.38, and in the ethylene molecule, 2.0. Therefore, internal rings of tri- and tetracyclic hydrocarbons approach olefins in the reactivity in hydrogenation.

Neurock et al. examined the differences in the reactivity of aromatic hydrocarbons [93] and determined the correlation [94] between the previously found transition state parameters (index of first-order valent molecular bonding, proton affinity, π -electron density) and the substrate reactivity. The correlation

of the π -electron density with the saturation kinetics of aromatic hydrocarbons was the most versatile [94]. The π -electron density was determined for each molecular fragment that can potentially undergo hydrogenation [85, 93, 95–97]; the fragment with the highest π -electron density was considered to be kinetically significant.

The correlation between the π -electron density with the saturation kinetics of aromatic hydrocarbons (Fig. 5) corresponded to the following equation:

$$\log k = A + B(\pi),$$

where $A = 155.66 \pm 34.12$ and $B = 151.23 \pm 33.88$.

Such correlation between the reaction rate constant and π -electron density can be attributed to the Coulomb attraction between the carbon fragment in an aromatic ring and the attacking agent [83, 94].

The hydrogenation rate constants for separate rings in molecules of mono-, bi-, tri-, and tetracyclic aromatic hydrocarbons are given in [84, 93]. The reactions were performed under the following conditions: 350°C, 6.8 MPa, CoMo/Al₂O₃ catalyst, pressure vessel. Below we consider the specific features of hydrogenation and hydrocracking of separate PCAs on nickel/cobalt tungsten/molybdenum sulfide catalysts.

Naphthalene and alkylnaphthalenes. The hydrogenation rate of the first ring in the naphthalene molecule considerably exceeds the hydrogenation rate of monoaromatic hydrocarbons. Tetralin is hydrogenated somewhat faster than *o*-xylene, despite similar position of the alkyl substituents in the aromatic ring. This fact can be attributed to the additional electron-donor effect of the naphthene ring or to acceleration of the adsorption on the active sites of the catalyst. On the whole, alkyl-substituted aromatic hydrocarbons can be hydrogenated on unsupported nickel–tungsten sulfide catalysts both faster and more slowly than the unsubstituted homologs, as demonstrated in [98, 99] by the example of mono-, bi-, and trimethylnaphthalenes. In this case, the reactivity depends on two competing factors: electron-donor effect of substituents and steric hindrance arising in adsorption of the molecule on active sites of the catalyst [83]. Specifically the latter factor is responsible for a decrease in the hydrogenation rate with increasing chain length. As shown in [98], close location of alkyl substituents (e.g., 1,8- and 2,3-dimethylnaphthalenes) and their presence in both rings (1,6- and 2,6-dimethylnaphthalenes) cause stronger hindrance to adsorption of the molecule on the

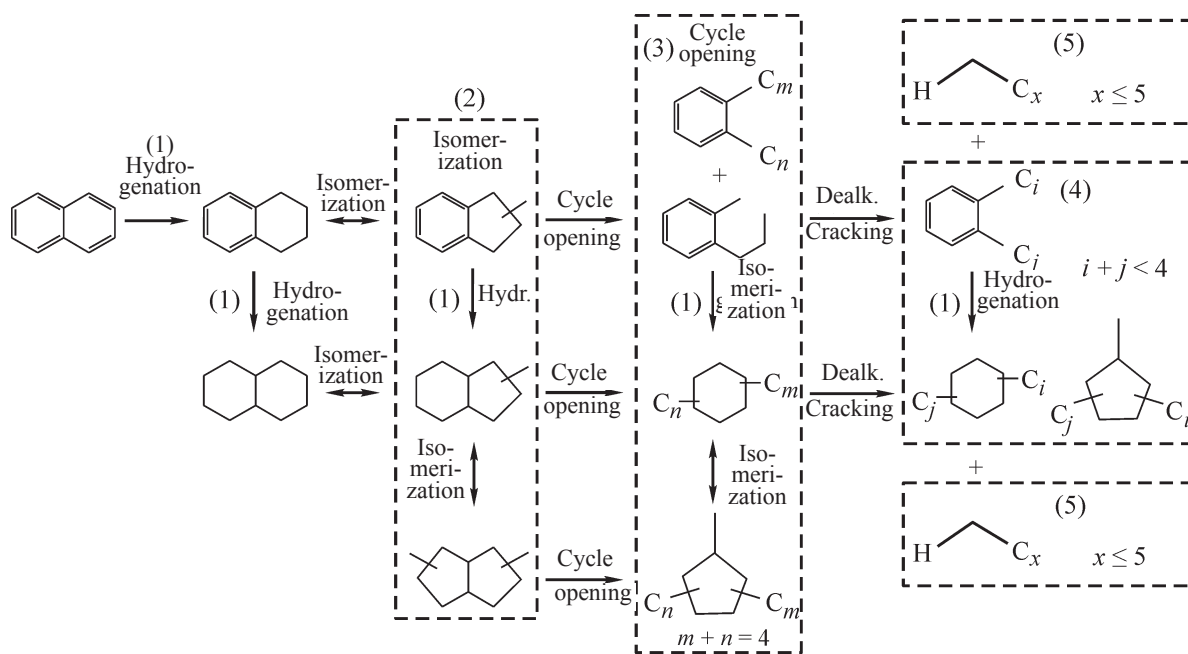


Fig. 6. Processes occurring in the course of hydrogenation–hydrocracking of naphthalene.

active site of the catalyst, which leads to low conversion to complete hydrogenation products. The ring without alkyl substituents is hydrogenated first, which is due to the absence of steric hindrance.

Naphthalene is relatively readily hydrogenated to tetralin, but its further conversion to decalins is hindered [100, 101] because of possible reverse dehydrogenation of tetralin, exhibiting donor properties, to naphthalene. The influence of temperature (350, 400, 450°C) on the conversion of naphthalene to tetralin was considered in [102]. At 450°C, tetralin cracking and isomerization products are detected in the reaction mixture in the total concentration not exceeding 5 wt %. At 400 and 450°C, the reaction equilibrium is attained in 60 min after the reaction start. The conversion to tetralin is more complete at 400°C. At 350°C, the equilibrium is not attained; 180 min after the start of the reaction, the naphthalene conversion to tetralin is about 72%. These data confirm that dehydrogenation is the main reaction only at high temperatures (>450°C) [33].

Hydrogenation–hydrocracking of naphthalene on nickel–tungsten sulfide catalyst supported on γ -Al₂O₃ was considered in [102]. In the presence of an acid component, the naphthalene hydrogenation to tetralin and decalin is accompanied by such side processes as ring opening, isomerization, dealkylation, and

cracking (Fig. 6). The hydrogenation followed by isomerization yields methylindans, methylhydrindans, and dimethylpentalanes. The subsequent ring opening yields dialkylbenzenes and dialkylcyclohexanes, which, in turn, isomerize into trialkylcyclopentanes. The dealkylation and cracking reactions occurring in the subsequent steps yield light paraffins, and also dimethylcycloalkanes and trimethylcyclopentanes with shorter-chain alkyl substituents.

Phenanthrene. Early studies of phenanthrene hydrogenation have shown that all the reactions in the phenanthrene hydrogenation system are reversible [84, 103]. Hydrogenation of the internal ring of phenanthrene is more favorable kinetically than hydrogenation of the external rings [84]. The primary hydrogenation products are di- and tetrahydrophenanthrene; with the progress of the reaction, they are hydrogenated to octahydrophenanthrene and, to a lesser extent, to perhydrophenanthrene. It should be noted that, in the initial period of dihydrophenanthrene hydrogenation, the selectivity with respect to phenanthrene is almost 100%, whereas the selectivity with respect to the tetra- and octahydro derivatives is close to zero, which is caused by thermodynamic factors. Therefore, Korre et al. [84] concluded that the phenanthrene hydrogenation starts with a fast reversible reaction

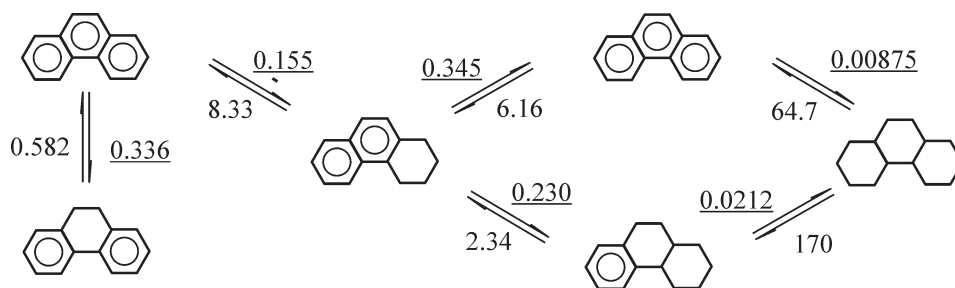


Fig. 7. Transformation scheme and rate constants of phenanthrene hydrogenation reactions (350°C, 6.8 MPa, CoMo/Al₂O₃, pressure vessel) [84].

yielding dihydrophenanthrene without its subsequent transformation into deep hydrogenation products. Similarly, in anthracene hydrogenation, an increase in the temperature over 340°C leads to a decrease in the concentration of dihydroanthracene in reaction products and to an increase in the concentration of the tetra- and octahydro derivatives; the reversible reaction between di- and tetrahydroanthracene to form anthracene and the octahydro derivative is possible. That is, dihydroanthracene exhibits hydrogen-donor properties [104]. The phenanthrene transformation scheme and the corresponding rate constants are given in Fig. 7 [84, 105].

Hydrogenation of octahydrophenanthrene occurs at a higher rate than that of tetralin; as in the case of tetralin and *o*-xylene, this fact suggests favorable effect of the naphthene ring on adsorption [106]. The external ring of tetrahydrophenanthrene is hydrogenated faster than the internal ring (Fig. 7), which is also due, most probably, to the steric factors.

The influence of temperature, pressure, and substrate–catalyst contact time on the phenanthrene hydrogenation on CoMo/Al₂O₃ was evaluated [89]. An increase in the hydrogen pressure in the system favors the reaction. The selectivity of the phenanthrene conversion to 1,8- and 1,10-octahydrophenanthrene considerably increases, whereas the selectivity with respect to 9,10-dihydrophenanthrene and tetrahydrophenanthrene somewhat decreases.

Elevation of temperature favors an increase in the phenanthrene conversion. In addition, with increasing temperature the selectivity with respect to 9,10-dihydrophenanthrene and 1,10-octahydrophenanthrene increases, that with respect to tetrahydrophenanthrene decreases, and that with respect to 1,8-octahydrophenanthrene

first increases and then decreases. With an increase in the substrate–catalyst contact time, the conversion increases. The selectivity of phenanthrene hydrogenation to 1,8- and 1,10-octahydrophenanthrene increases also, whereas for 9,10-dihydrophenanthrene and tetrahydrophenanthrene the selectivity decreases [89].

The rate constants of all the reactions occurring with phenanthrene on the CoMo catalyst, the activation energies, and adsorption constants were estimated using the Broyden–Fletcher–Goldfarb–Shanno algorithm [89]. The calculated values for various reaction schemes were close to the experimental values. Comparison of the rate constants for various phenanthrene hydrogenation schemes clearly showed that the rate constant of transformation of 9,10-dihydrophenanthrene to tetrahydrophenanthrene was considerably lower than the rate constants of the other reactions. The actual reaction rate was equal to the rate constant multiplied by the hydrogen partial pressure. With the effect of the hydrogen partial pressure taken into account, the difference between the reaction rates became still larger with increasing pressure. Thus, it can be concluded that the transformation of 9,10-dihydrophenanthrene into tetrahydrophenanthrene can be neglected.

Anthracene. The scheme of anthracene hydrogenation is similar to that of phenanthrene hydrogenation. The relationships are also similar, but there are certain differences. The rate of the first hydrogenation steps (to di- and tetrahydroanthracene) is higher compared to phenanthrene hydrogenation because of lower conjugation energy of anthracene. However, the hydrogenation of tetra- and octahydroanthracene occurs, on the whole, at a lower rate than that of tetra- and octahydrophenanthrene. As octahydro derivatives are accumulated in the reaction mixture at temperatures higher than 430°C, the

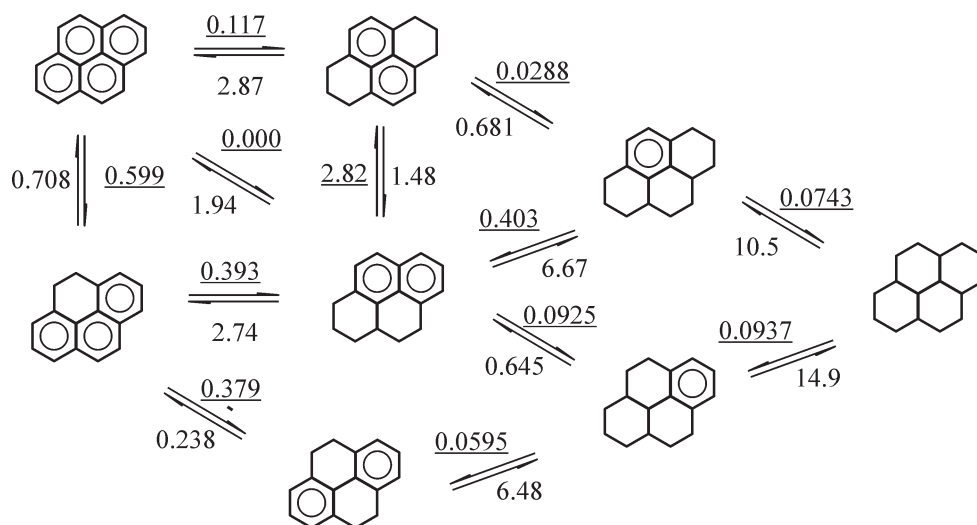


Fig. 8. Transformation scheme and rate constants of pyrene hydrogenation reactions (350°C, 6.8 MPa, CoMo/Al₂O₃, pressure vessel) [84].

contribution of reactions involving opening of the external saturated ring to form alkylnaphthalenes increases [107].

Pyrene. The transformation scheme and rate constants of pyrene hydrogenation are shown in Fig. 8 [84]. The central ring is hydrogenated at the highest rate. In the phenanthrene fragment formed, the hydrogenation rate of the central ring is approximately equal to the hydrogenation rate of the central ring in phenanthrene itself. The hydrogenation of the external ring of dihydropyrene occurs faster than the formation of tetrahydrophenanthrene from phenanthrene. As seen from Fig. 8, the hydrogenation rate of a,s-hexahydropyrene (two fused naphthene rings in the molecule) is 14 times higher than the hydrogenation rate of s-hexahydropyrene (the naphthene rings are not fused). In the a,s-isomer, the internal ring is hydrogenated 4.4 times more slowly than the external ring. This may be caused by steric hindrance to adsorption of 2-hexahydropyrene in one plane on the catalyst surface. It should be noted that decahydropyrene dehydrogenation reactions are thermodynamically more favorable under the conditions studied (350°C, 6.8 MPa).

Chrysene. The primary products of chrysene transformations are di- and tetrahydrochrysene. Hydrogenation of dihydrochrysene follows the pathway of saturation of the naphthalene moiety, and hydrogenation of the isolated benzene ring occurs at an extremely low rate, which is characteristic of such structures [84]. Hydrogenation of the external ring of hexahydrochrysene is preferable compared to the

hydrogenation of the internal ring. Similarly to pyrene, saturation of the external ring of a,s-octahydrochrysene occurs at a considerably (24 times) higher rate compared to the s-isomer.

Fluoranthene. The major primary product of fluoranthene hydrogenation, tetrahydrofluoranthene, transforms into a,s-decahydrofluoranthene (with fused six-membered naphthene rings) and, to a considerably lesser extent (at 14 times lower rate), into s-decahydrofluoranthene (in which the six-membered naphthene rings are not fused) [108]. The reactivity of fluoranthene in hydrogenation is higher than that of phenanthrene (by a factor of 4) and pyrene (by a factor of 1.2), and tetrahydrofluoranthene is 3 times more reactive in hydrogenation than naphthalene [109]. This fact can be attributed to unique structure of the fluoranthene molecule containing the five-membered ring.

Fluoranthene, compared to other PCAs, readily undergoes hydrocracking to yield 1- and 2-phenyltetralin, tetralin, and benzene as major products. High reactivity of PCAs containing a five-membered ring in the molecule (fluorene, fluoranthene) requires their consideration as a separate class of compounds when analyzing the kinetic relationships of hydrogenation of PCA mixtures [109].

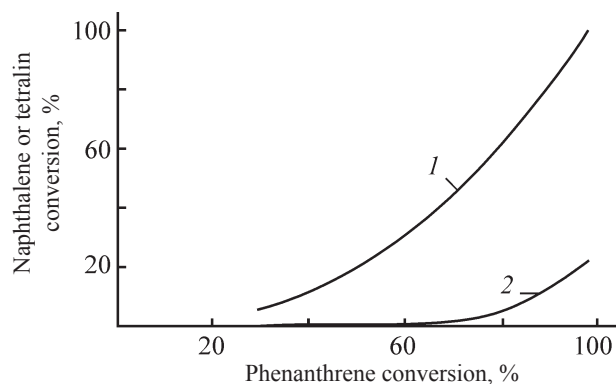
With the PCA-containing feed, hydrogenation can be accompanied by accumulation of hexa- and heptacyclic aromatic hydrocarbons in the recirculating gas oil (if the process is performed with recirculation) and by coking of the catalyst and apparatus, which is associated with low accessibility of catalyst pores to bulky CPA molecules and low solubility of these compounds in the feed. Thus,

Table 4. Constants of adsorption of hydrocarbons with different numbers of aromatic rings on CoMo/Al₂O₃ catalyst [84]

Hydrocarbon/group of hydrocarbons	<i>K</i> , L mol ⁻¹
Pyrene	38.5
Chrysene	38.5
Tricyclic aromatic	17.5
Bicyclic aromatic	7.7
Monocyclic aromatic	7.4
Saturated	3.9

these compounds have no time for hydrogenation and participate in free-radical condensation [110]. High-molecular-mass products can be formed via ortho and peri condensation. Ortho condensation, i.e., addition of four carbon atoms to the region of the highest π localization, is kinetically preferable, whereas peri condensation is more favorable thermodynamically. Sullivan et al. [110] analyzed the composition of recirculating streams and deposits in air-cooled apparatuses of hydrocracking installations and concluded that the peri condensation pathway is preferable.

The above-considered kinetic relationships of PCA hydrogenation are given for individual chemicals. In practice, the highly aromatic feedstock contains a wide spectrum of aromatic hydrocarbons differing in the number of rings and in the length, position, and number of alkyl substituents. In addition, the feedstock usually contains sulfur, oxygen, and nitrogen compounds.

**Fig. 9.** Conversion of (1) naphthalene and (2) tetralin as a function of phenanthrene conversion in their ternary mixture [112] (for conditions, see Table 5).

Because of competition for active sites of the catalysts, certain compounds will inhibit transformations of other compounds, which should be taken into account when formulating the feedstock. For example, as shown in [111], phenanthrene inhibits the naphthalene hydrogenation. As the phenanthrene content in its binary mixture with naphthalene is increased from 5.3 to 70%, the naphthalene conversion decreases from 96 to 86%, whereas the phenanthrene conversion does not change noticeably. This is due to the fact that the adsorption constants on catalyst active sites increase with the number of aromatic rings in the molecule [84, 111]. In particular, the ratio of the phenanthrene and naphthalene adsorption constants on hydrogenating and acid sites (NiW/Y catalyst, 6.8 MPa, 350°C) is 1.9 and 3.9, respectively [111]. The adsorption constants of hydrocarbons with different numbers of aromatic rings are given in Table 4 (CoMo/Al₂O₃ catalyst, 350°C, 6.8 MPa) [84].

Thus, the general trend in hydrogenation of multicomponent PCA mixtures is inhibition of the hydrogenation of hydrocarbons with a smaller number of aromatic rings by hydrocarbons with a larger number of aromatic rings, due to competition for active sites. This trend is characteristic both of sulfide catalysts and of nonsulfidized noble metals [81, 112]. On the whole, hydrogenation of monocyclic hydrocarbons and tetralin in multicomponent mixtures is the most hindered. This is clearly seen from Table 5 [112], where the conversions of phenanthrene, naphthalene, and tetralin, taken separately (5% solution in dodecane) and in a mixture (5% phenanthrene, 10% naphthalene, 25% tetralin, 60% dodecane), are compared. As can be seen, in the ternary mixture the phenanthrene conversion decreases by 25%; the naphthalene conversion, by a factor of 2.5; and the tetralin conversion, by a factor of 50. Correspondingly, the tetralin hydrogenation can start after almost complete consumption of phenanthrene. This is illustrated by Fig. 9 [112]. As can be seen, the tetralin hydrogenation starts when the phenanthrene conversion reaches 75%. Favorable hydrogenation conditions (high pressure, low feed space velocity, relatively low temperature) level off the differences in the conversion of hydrocarbons with different number of aromatic rings [81].

Korre et al. [84] studied in detail the inhibition of the hydrogenation of *o*-xylene, naphthalene, phenanthrene, pyrene, and chrysene in five model quinary mixtures differing in the content of these hydrocarbons. The

Table 5. Conversion of phenanthrene, naphthalene, and tetralin taken separately and in the ternary mixture [112] (PtPd/Al₂O₃ catalyst, 3.4 MPa, 300°C, space velocity 100 h⁻¹, H₂ : feed 11 : 1)

Hydrocarbon	Conversion of individual reactant, %	Conversion in ternary mixture, %
Phenanthrene	81.5	60.0
Naphthalene	85.1	32.0
Tetralin	50.9	1.0

conversion of each hydrocarbon in the five mixtures was considered as a function of the reaction time (350°C, 6.8 MPa, CoMo/Al₂O₃). The main conclusion following from the data obtained is that the hydrogenation rate of tetracyclic aromatic hydrocarbons is virtually independent of the mixture composition; that of tricyclic hydrocarbons decreases as the mixture is made heavier; and that of mono- and bicyclic hydrocarbons considerably decreases in going from mixtures in which bicyclic hydrocarbons prevail to mixtures containing 35–45% tetracyclic hydrocarbons. The naphthalene hydrogenation is significantly influenced by the total content of tri- and tetracyclic aromatic hydrocarbons in the mixture. In phenanthrene hydrogenation, the maximal conversion is observed in the mixture with the highest naphthalene content. The rate of consumption of tetraaromatic hydrocarbons, in contrast to that of tricyclic aromatic fragments, is independent of the mixture composition. This effect is still more noticeable for bicyclic aromatic fragments.

Along with mutual inhibition of the hydrogenation of aromatic hydrocarbons, inhibition with heteroatomic compounds should be taken into account. It is well known that ammonia, one of hydrodenitrogenation products, deactivates both acid and hydrogenating sites of the catalyst, with the acid sites deactivated to a greater extent [112]. Therefore, the profile of PCA transformation products changes: The fraction of hydrogenation products increases, and that of hydrocracking and polycondensation products decreases.

Organic nitrogen organic compounds, especially basic compounds (e.g., quinoline), are stronger inhibitors than ammonia [113]. The inhibiting effect is manifested to a greater extent in early steps of the reaction, when quinoline and hydroquinolines have not yet transformed into other nitrogen compounds. The conversions in PCA hydrogenation, dibenzothiophene hydrodesulfurization, and dibenzofuran hydrodeoxygenation in model

mixtures containing organic nitrogen compounds and free of them are given in Table 6 [109]. As can be seen, nitrogen-containing compounds inhibit all the reactions except dibenzofuran deoxygenation. The latter can be attributed to the experiment uncertainty because of extremely low conversion. As reported in [113], quinoline significantly inhibits the hydrodeoxygenation of phenols, benzofuran, and dibenzyl ether.

Oxygen-containing compounds exert a weak inhibiting effect on the desulfurization and hydrogenation [113]. For example, in the presence of 0.683 mM tetrahydronaphthol, the rate constant of hydrogenation of phenanthrene to dihydrophenanthrene decreases by a factor of only 1.03; that of hydrogenation of fluoranthene to tetrahydrofluoranthene, by a factor of 1.005; and that of transformation of dibenzothiophene into cyclohexylbenzene, by a factor of 1.52 [109].

The inhibiting effects are studied most frequently in binary, ternary, and quaternary model mixtures. There are virtually no studies dealing with competition for active sites and mutual inhibition in multicomponent mixtures containing PCAs with different numbers of rings and sulfur-, oxygen-, and nitrogen-containing organic compounds. Only relative transformation rates for some of these compounds were determined (Table 7 [114]) without their comparison with the transformation rates of the same compounds taken separately.

There are no data on hydrogenation competition in mixtures of alkyl-substituted and unsubstituted PCAs, although such mixtures are real feedstock. For example, mixtures of catalytic cracking gas oil with coal tar (1 : 1), used in the United States for producing JP-900 fuel [115], have such composition, but the mutual influence of the mixture components on the progress of hydrogenation, hydrocracking, and hydrodesulfurization (-denitrogenation, -deoxygenation) was not examined. No studies were aimed at optimization of the fractional composition of such feedstock from the viewpoint of

Table 6. Conversion in hydrogenation, hydrodesulfurization, and hydrodeoxygenation of the feedstock containing nitrogen-containing compounds and free of them [109]. Conditions: 350°C, 17.1 MPa, 0.99 h⁻¹ with nitrogen-containing compounds and 0.84 h⁻¹ without them, NiMo/γ-Al₂O₃)

Composition of model mixed feedstock		
component	concentration, mM	
Quinoline	0.168	None
Acridine	0.146	"
Indole	0.243	"
5,6,7,8-Tetrahydro-1-naphthol	0.654	0
Dibenzofuran	0.382	0.379
Dibenzothiophene	0.196	0.204
Phenanthrene	1.36	1.35
Fluoranthene	2.06	2.02
Pyrene	0.684	0.697
Conversion, %		
Dibenzofuran hydrodeoxygenation	4.12	2.83
Dibenzothiophene hydrodesulfurization	13.1	33.9
Phenanthrene hydrogenation	9.93	33.1
Fluoranthene hydrogenation	41.7	65.6
Pyrene hydrogenation	20.3	37.7

eliminating to a maximum possible extent the inhibition of the hydrogenation of bi- and tricyclic PCAs by hydrocarbons containing a larger number of rings.

These gaps are partially associated with the limited possibilities of the analytical techniques available in the 1970–1990s for studying multicomponent hydrocarbon mixtures. Attempts were made to distinguish structural groups in the feed and products using a set of methods including ¹H and ¹³C NMR spectroscopy, IR spectroscopy, and elemental analysis [116, 117]; this allowed monitoring the variation of the content of separate groups, e.g., aliphatic sulfides, Ph–OH, –COOH, etc., in the process. However, this approach involves problems with interpretation of the IR and NMR spectra of multicomponent mixtures and furnishes information on the content of structural groups, rather than on the content of particular components (e.g., ethylnaphthalenes) in the mixture. Today, two-dimensional gas chromatography–mass spectrometry

offers wide possibilities for analyzing the mutual effect of the components in processing of multicomponent mixtures [118, 119]. In particular, it allows monitoring changes in the content of hydrocarbon groups (e.g., of naphthoaromatic tricyclic hydrocarbons with one aromatic ring) with different numbers of carbon atoms in the molecule. For example, Hamilton et al. [119] studied by this method the coal liquefaction products before and after hydrocracking.

Thus, the use of modern analytical methods with appropriate experiment design can become a route to studying the mutual effect of the components in hydroprocessing of complex mixtures. This, in turn, will allow substantiated choice of the feed containing essentially different components (heavy distillates of coal origin, containing unsubstituted tri- and tetracyclic PCAs; LGCC with high content of alkylnaphthalenes; pyrolysis tar containing naphthalene as the major component) and of its fractional composition.

Table 7. Relative rate constants of compound transformations in a mixture [114]. Conditions: 344°C, 4.8 MPa, CoMo catalyst; mixture composition: 2 mol of 2-methylnaphthalene, 1.5 mol of n-hexadecane, and 1 mol of each of the other components

Compound	Rate constant relative to naphthalene ^a
2-Methylnaphthalene	1.0
2,3-Dimethylnaphthalene	1.4
Dibenzothiophene	3.6
Benzothiophene	3.4
Thiophene	≥10
Indole	0.9
<i>o</i> -Ethylaniline	1.1
Quinoline	1.3
2,3-Benzofuran	1.0
<i>o</i> -Ethylphenol	1.2
Dibenzofuran	0.4
2-Phenylphenol	1.4
<i>cis</i> -2-Phenyl-1-cyclohexanol	≥10
<i>p</i> -Cresol	5.2

^a The rate constant of naphthalene hydrogenation was taken as unity.

CATALYSTS FOR HYDROPROCESSING OF HIGHLY AROMATIC WASTES TO OBTAIN FUEL FRACTIONS

The possibility of hydrogenation of coal coking tar as a method for producing high-boiling hydrocarbon solvents was demonstrated in the United States as early as the 1940s [120]. The process was performed in two steps and consisted in liquid-phase hydrogenation of the tar as a whole in the first step and gas-phase hydrogenation of the 210–300°C fraction in the second step. A molybdenum-containing catalyst was used. The hydrogenation of coking tars and coal liquefaction distillates was later considered as a promising process for producing fuel components.

The CoMo, NiMo, and NiW sulfide catalysts traditionally used in oil refining for hydrodesulfurization and hydrodearomatization are used for the above purpose most widely. The active phase of NiMoS, CoMoS, or NiWS consists of molybdenum or tungsten disulfide clusters with promoter atoms on faces. The structure of

Table 8. Variation of the properties of the CoMo/ γ -Al₂O₃ catalyst along the bed height [129]

Catalyst sampling point	Content in catalyst, wt %		Specific surface area, m ² g ⁻¹
	carbon	iron	
Fresh catalyst	0	0.1	158
Upper part of reactor	5.9	13.5	99
1/3 of height from the top	14.4	1.3	74
2/3 of height from the top	14.1	0.2	84
Lower part of reactor	5.7	0.2	105

the active phase of sulfide catalysts is described in detail in a number of papers, e.g., in [121–123]. The catalyst activity and resistance to poisons depends on the surface area, pore size, promoter used, and support acidity [124].

Catalysts with narrow pores are rapidly deactivated under the conditions of hydrotreating of distillates originating from coal because of the deposition of coke and metals. The catalyst deactivation and coking are caused by specific composition of the feedstock: presence of basic nitrogen-containing organic compounds, phenols, PCAs, and asphaltenes. The formation of coke-like substances on the catalyst surface is enhanced with the support acidity [124, 125]. This is due to the adsorption on catalyst acid sites of basic nitrogen-containing compounds, followed by their dehydrogenation and polycondensation to form coke deposits. An important parameter of the feed, influencing the amount of coke deposits, is the feedstock coke residue. For coal-derived distillates, it can reach 31% [126], whereas for petroleum vacuum distillates it does not exceed 1% [127].

As noted in Section 2, in processing of feedstock with high content of basic nitrogen, acid sites are deactivated to a greater extent, which leads to a decrease in the overall feedstock conversion and in the yield of light distillates, e.g., of the gasoline fraction (Fig. 10) [128]. The possible way of preventing the catalyst coking caused by basic nitrogen-containing compounds is the use of supports of lower acidity or intentional introduction of acidity-reducing modifiers (e.g., CaO) into the support [125].

The deposition of metals (Na, K, Fe, Ca, Ti, etc.) is another cause of catalyst deactivation. Whereas

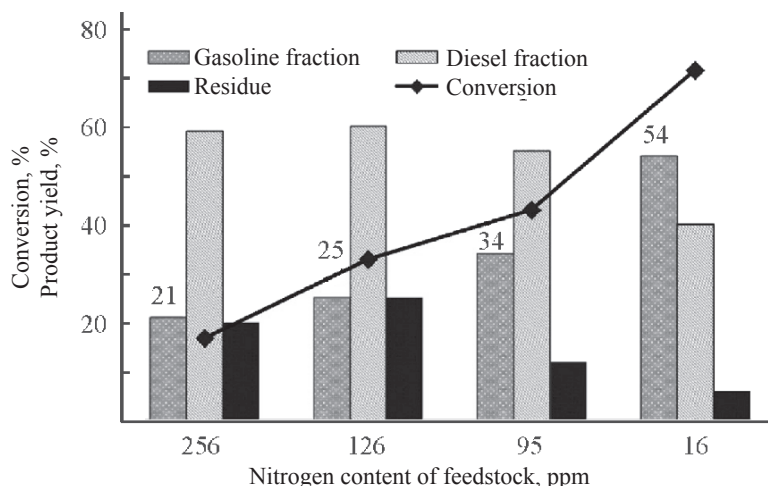


Fig. 10. Influence of the nitrogen content of the feedstock on the conversion and product yield in hydrocracking (10 MPa, 400°C, 0.53 h⁻¹, NiW/USY catalyst) [128].

coke deposits can be removed by firing, the deposited metals poison the catalyst irreversibly. Table 8 shows as example how the properties of the CoMo/ γ -Al₂O₃ catalyst vary along the bed height after continuous operation of the reactor for 150 h in hydrofining of lignite semicoking tar (Conradson carbon residue 3%) [129]. The coke deposits are characteristic for catalyst

bed layers with the highest temperature created by exothermic hydrogenation reactions. The major fraction of iron is deposited on the catalyst at ~250°C. Coking decreases the catalyst surface area, but after regeneration it is restored. However, high iron content prevents the restoration of the surface area to values characteristic of the fresh catalyst.

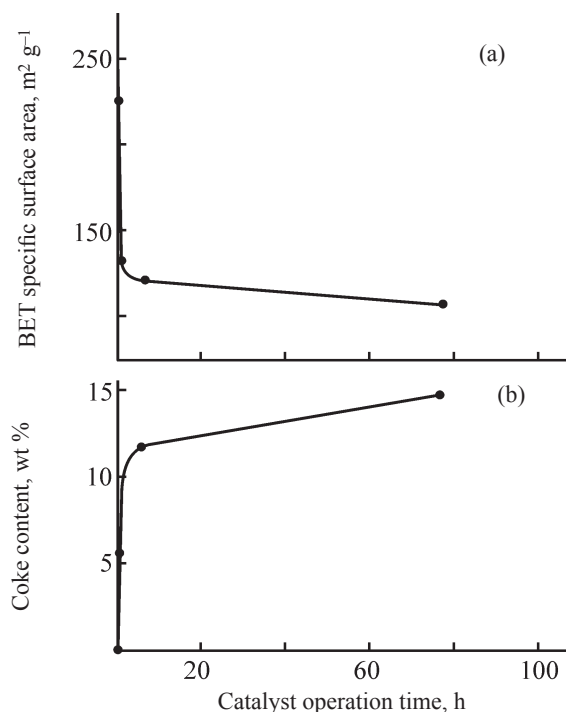


Fig. 11. (a) Specific surface area and (b) amount of coke deposits for NiMo catalyst BASF MS-21 as functions of the time of its operation in a reactor for hydrofining of coal pyrolysis distillate [130].

Figure 11 shows that the catalyst surface area decreases most rapidly in the first 10–20 h of its operation, because the largest amount of coke deposits is formed specifically in the first hours of the catalyst operation, after which the catalyst activity decreases insignificantly and soon becomes practically constant. The major amount of coke is formed in micropores of radius less than 6 nm [130].

The catalyst deactivation is accompanied, along with a decrease in the specific surface area, by agglomeration of molybdenum disulfide crystallites and degradation of the catalytically active NiMoS phase [131]. The agglomeration is caused by the action of high temperature in local overheating zones, and degradation of the sulfide phase, by occupation of vacant sulfur bonds on faces of MoS₂ crystallites with asphaltene precursors containing polar –OH, –NH₂, and –COOH groups.

The problem of the catalyst deactivation may be solved by using catalysts with wide pores, which are not plugged by asphaltene molecules. Studies [88, 132] of the activity of NiW catalysts on SBA-15 support with different pore size (pore diameter 5.4, 7.1, and 15.7 nm) in hydrotreating of the coal liquefaction product have shown that the degrees of denitrogenation

and dearomatization considerably increase with the pore size. For example, the degree of denitrogenation on the catalyst with the pore diameters of 5.4 and 15.7 nm is 15 and 40%, respectively. However, unfortunately, catalysts with larger pore diameters were not studied in this respect, which does not allow evaluation of the optimum pore diameter in a catalyst for processing coal-derived distillates.

The use of various approaches to the problem of coke deposition, however, does not solve the problem of deactivation with metals. Therefore, treatment of coal-derived distillates in steps is a more efficient approach [126, 130, 133]. In this case, a cheap, readily available catalyst (e.g., sulfidized iron wire) can be used in the first step, and NiMo and NiW sulfide catalysts, in the second step. The goal of the first step is removal of coke precursors, oxygen- and nitrogen-containing compounds, and ash impurities. By performing the first step at a temperature of 410–425°C, a pressure of 13.8 MPa, and a space velocity of 0.6 h⁻¹, the coke residue of coking tar can be decreased from 30 to 18%, the oxygen content, from 10 to 5%, and the ash residue, from 1.2 to 0.08%; the viscosity also significantly decreases. However, denitrogenation does not occur under such conditions. The feedstock pretreatment in the first step ensures the constant catalyst activity (degrees of desulfurization and denitrogenation, H/C ratio in the product) in the second step and high efficiency of the process as a whole (the degree of removal of oxygen and sulfur is 90–100 and 88–89%, respectively; the aromaticity decreases by a factor of 1.6, according to ¹³C NMR data) [126]. The implementation of processes for producing fuel distillates from pyrolysis and coal coking distillates, pyrolysis tar, etc., is considered in detail in the next section; here we only briefly mention the catalysts used and describe changes in their properties due to deactivation.

The process suggested in patent [134] involves in the first step tar hydrocracking at high temperature (415–450°C) and pressure (13.6 MPa) on NiMo/Al₂O₃ (CoMo/Al₂O₃) sulfide catalyst; this is followed by two-step fining of the hydrocracking distillates on similar catalysts, but at lower temperatures: 340–370 and 320–340°C. Apparently, because of extremely low acid properties of the hydrocracking catalyst used, the ring opening mainly occurs by the free-radical mechanism owing to high temperatures.

The use of zeolite-containing hydrocracking

catalysts with strong acid properties in the first step (e.g., of NiW/USY) will inevitably lead to serious coking and deactivation with nitrogen bases. Therefore, it is not appropriate to perform hydrocracking prior to hydrofining of coal-derived distillate. Loading wide-pore NiMo/Al₂O₃ demetalation catalyst into the reactor in the first step and performing the process at a moderate temperature (280°C, 10 MPa, 0.5 h⁻¹) ensure 89.5% demetalation along with 57% conversion of asphaltenes [128]. Visual analysis of images of the spent demetalation catalyst, taken by scanning electron microscopy in combination with energy-dispersive X-ray spectrometry (SEM-EDX), shows that iron and calcium are uniformly distributed throughout the particle surface, whereas carbon is concentrated to a greater extent on the external surface of the particle.

Hydroprocessing in slurry reactors using nanoheterogeneous catalysts prepared in situ from precursors in the reaction medium can be an alternative to the two-step processing of coal-derived distillates [135–139]. The advantages of hydrocracking with supported catalysts dispersed in the feedstock include solution of the problem of the catalyst poisoning and coke deposition in the pores, so that it becomes possible to process the least favorable feedstock with high content of catalytic poisons without preliminary treatment, and also high area of the catalytic surface and reduced diffusion restrictions, which is particularly important for bulky PCA molecules. Despite extensive studies on nanoheterogeneous catalysis of hydrocracking of petroleum residues by metal sulfides, there are only a few papers in which the use of unsupported catalysts in treatment of highly aromatic distillates is suggested [98, 99, 140].

As the hydrofining conditions are made more severe (elevation of temperature and pressure, decrease in the space velocity), the content of heteroatoms in the products decreases [141], and the content of paraffin-naphthene hydrocarbons and H/C ratio increase [142], the yield of the light fraction (boiling range up to 200°C) increases, and the yield of the residue boiling above 325°C decreases, whereas the selectivity with respect to medium-temperature distillate does not change noticeably. However, thermodynamic limitations of the PCA hydrogenation reactions should be taken into account. As shown in [34], as the temperature of hydrotreating of the semicoking tar fraction boiling up to 300°C is increased from 350 to 400°C, the content of

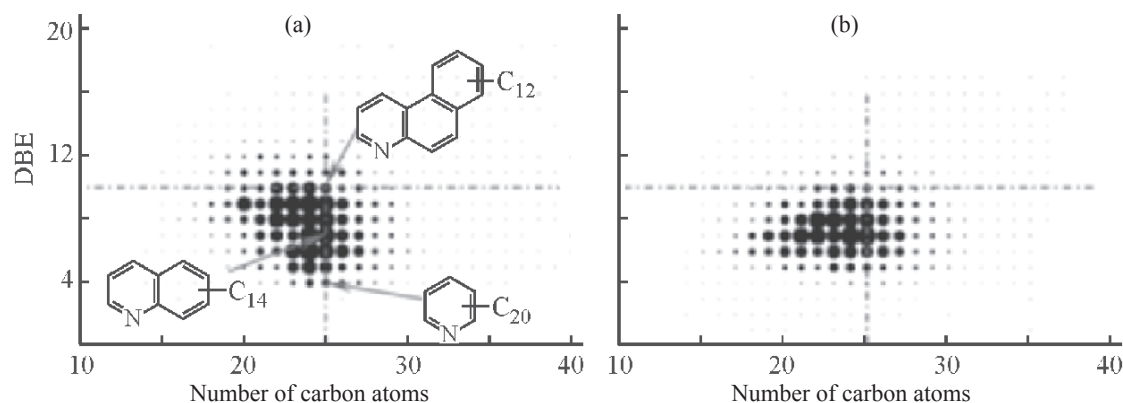


Fig. 12. Distribution of nitrogen-containing compounds in coking gas oil with respect to the number of carbon atoms and DBE (a) before and (b) after hydrotreating [74].

naphthenes in the product decreases from 29 to 14%, and the content of aromatic hydrocarbons proportionally increases. However, the temperature elevation favorably influences the conversion of oxygen-containing compounds. The content of aromatic hydrocarbons in the gasoline fraction and, correspondingly, its cetane number decrease with increasing pressure, but, apparently, the cetane number of the diesel fraction increases owing to more complete conversion of aromatic hydrocarbons [143].

Even under severe conditions, hydrodesulfurization of sterically hindered dibenzothiophenes and alkyldibenzothiophenes occurs incompletely, and residual amounts of these compounds are present in the product [72] (see Appendix, Fig. A4). Polycyclic nitrogen-containing compounds undergo hydrogenation without denitrogenation, so that DBE decreases, but the distribution with respect to the number of carbon atoms remains unchanged [74] (Fig. 12).

Modification of NiMo/Al₂O₃ and NiW/Al₂O₃ catalysts with phosphorus slightly increases the pore size, favors uniform distribution of Mo (W) and Ni over the support surface, weakens the interaction of the metal with the support, and decreases the temperature at which the oxide phase is reduced with hydrogen [144, 145]. In addition, the concentration of weak and medium-strength acid sites increases, which enhances the catalytic activity in hydrocracking.

Zeolite-containing catalysts, in particular, zeolites Y, are widely used in the hydrocracking step [128, 146, 147]. Because basic nitrogen compounds deactivate zeolite-containing catalysts, the nitrogen content of the feed for hydrocracking on supported catalysts should

not exceed 10 ppm, which is reached only in two-step hydrofining. In hydroprocessing of coal-derived distillates, denitrogenation is one of the most difficultly occurring reactions. The conversion products contain alkyl-substituted ammonium salts and hydrogenated derivatives of quinolines, isoquinolines, and acridines [148]. The naphthene ring opening, isomerization, and dealkylation reactions are intensified on zeolite catalysts.

According to [147], the *trans/cis*-decalin ratio in naphthalene hydrocracking products increases with an increase in the content of zeolite Y in the NiW/Al₂O₃-Y catalyst (and, correspondingly, with an increase in the catalyst acidity). This ratio increases from 4.2 for NiW/Al₂O₃ to 6.0 for NiW/Al₂O₃-Y containing 5% zeolite. This ratio of decalin stereoisomers is extremely important from the viewpoint of thermal stability of jet fuels, because *trans*-decalin considerably surpasses *cis*-decalin in the thermal stability [149]. Hydrocracking of long alkyl chains also enhances the thermal stability of the fuel, because alkanes and naphthenes with long alkyl substituents are more susceptible to cracking at high temperatures in fuel tanks.

Zeolite-containing catalysts can also be used for isomerization of a mixture of decalin stereoisomers into the *trans* isomer [150, 151]. It is suggested that the process be performed at 200–300°C under a hydrogen or nitrogen pressure using Pt (Pd) catalysts on zeolites (mordenite or USY). The maximal conversion (90–95%) is reached at 270°C; the selectivity with respect to *trans*-decalin in the temperature interval 210–270°C is 100%. The conversion and selectivity increase with the hydrogen pressure in the interval 1.3–2.4 MPa and then flatten out [151]. These catalysts can also be used

for selective hydrogenation of naphthalene into *trans*-decalin with the selectivity higher than 80% [150].

Aluminum–platinum [80] and aluminum–palladium [152] fluorinated catalysts containing ~1% fluorine are suggested as an alternative to zeolite catalysts for enhancing the hydrocracking and ring opening.

The following catalysts can be used in the first step of hydrotreating with the aim of denitrogenation and demetalation of the feed: iron sulfide [126, 130, 133], wide-pore nickel– and/or cobalt–molybdenum catalysts [153, 154], or sulfidized platinum or palladium [154] (when the feed contains olefins and dienes, which potentially cause formation of carbon deposits on the catalyst surface and on the apparatus walls due to polymerization). Noble metal sulfides are well known as catalysts of selective hydrogenation of olefins and dienes in gasoline fractions of secondary origin; the reaction is performed at moderate temperatures (180–280°C) [155]. However, these catalysts are virtually inactive in denitrogenation. As shown in [154], at a temperature of 315°C, a pressure of 13.6 MPa, and a feed space velocity of 1 h⁻¹, Shell 424 nickel–molybdenum catalyst ensures 77% denitrogenation of coal liquefaction distillate (0.3 wt % nitrogen), whereas platinum sulfide on activated charcoal (Engelhard) ensures only 13% denitrogenation. The degree of denitrogenation acceptable for the subsequent conversion of the product on a zeolite-containing catalyst (nitrogen content no higher than 10 ppm) is reached only under severe conditions (temperature higher than 375°C, space velocity 0.35–0.5 h⁻¹, pressure higher than 10 MPa) on a fresh highly active molybdenum- or tungsten-containing catalyst [156]. Denitrogenation of azaarenes is the most difficult; they are hydrogenated to form naphthoaromatic derivatives without nitrogen elimination.

Brief characteristics of the examined catalysts for hydrofining of liquid products of coal coking, pyrolysis, and hydroliquefaction are given in Table 9. Sulfide catalysts on neutral or acid supports are used most widely. Nickel, platinum, and palladium catalysts are active at moderate temperatures (150–200°C), but because of their deactivation with sulfur compounds they are hardly suitable for hydrogenation of coal-derived products; however, they can be used for hydrogenation of close-cut preliminarily hydrotreated fractions or for preliminary hydrofining of feedstock containing sulfur compounds, e.g., of pyrolysis tar [157]. Bagrii and Tsodikov [158] studied commercial nonsulfidized nickel catalyst in hydrogenation of acenaphthene and fluorene. Hydrogena-

tion of acenaphthene was performed at 200°C, 8 MPa, and 0.08–0.12 h⁻¹, and that of fluorene, at 150–160°C, 10 MPa, and 0.08–0.12 h⁻¹. The acenaphthene conversion was 100% with selective formation of decahydroacenaphthene, and the fluorene conversion was 100% with selective formation of dodecahydrofluorene. The fluorene hydrogenation product had the density of 945–950 kg m⁻³, boiling point of 254–258°C, and congealing point below –60°C; it can be considered as a component of high-density aviation fuels. One-step hydrogenation on Raney nickel at 300–350°C was suggested for producing components of high-density aviation fuel from reforming residues [80, 159].

Hydrofining of coking tars in supercritical hydrocarbon solvents, in particular, in xylene and light naphtha [160], is of interest. The function of the solvent consists in intensification of the mass transfer, dissolution of coke precursors, reduction of the concentration of free radicals in the system and, correspondingly, of the probability of their recombination with the formation of high-molecular-mass products. The dissolution of high-molecular-mass reaction participants and their diffusion to the catalyst surface are ensured at the optimum solvent/feed ratio and sufficient concentration of the reactants in the system.

As already noted [89], two-step processing of highly aromatic feedstock can be performed under milder conditions compared to one-step processing. As shown in [171], two-step processing can be implemented by arranging in one reactor two beds of different (hydrogenation and hydrocracking) catalysts. In so doing, the LGCC processing product will meet the requirements to jet fuel. Nevertheless, it seems more appropriate to use two reactors operating under the conditions optimum for the corresponding process. In this case, it is also possible to separate and decontaminate the gas phase from the flow of products from the first reactor to exclude the deactivation of the second-step catalyst with ammonia (and with hydrogen sulfide, when using platinum or palladium catalysts). In the next section, we will consider the suggested implementations of processes for treating highly aromatic distillates to obtain fuels.

IMPLEMENTATION OF PROCESSES FOR PRODUCING FUELS FROM HIGHLY AROMATIC WASTES

The choice of a procedure for processing of a highly aromatic feedstock is primarily based on its

Table 9. Brief characteristics of catalysts for hydrofining liquid products of coal coking, pyrolysis, and liquefaction

Feedstock	Optimum process conditions	Catalyst	Result	References
Low- and medium-temperature coking tar	Demetalation: 280°C, 10 MPa, 0.5 h ⁻¹ Hydrofining: 400°C, 10 MPa, 0.4 h ⁻¹ Hydrocracking: 400°C, 10 MPa, 0.53 h ⁻¹ (feedstock: residue from the second step)	Demetalation and hydrofining: NiMo/γ-Al ₂ O ₃ Hydrocracking: NiW/USY	Demetalation: degree of desulfurization, denitrogenation, and demetalation 15, 8.5, and 89.5%, respectively; asphaltene conversion 57% Hydrofining: degree of desulfurization 98.9%, degree of denitrogenation 91.8%, product contains 22% gasoline and 54% diesel fractions Hydrocracking: product contains 21% gasoline and 59% diesel fractions	[126, 130, 133]
S.B.–360°C fraction of coal tar	Hydrofining: 360°C, 8 MPa, 0.8 h ⁻¹ Hydrocracking: 380°C, 8 MPa, 0.8 h ⁻¹	Hydrofining: NiMo/γ-Al ₂ O ₃ Hydrocracking: NiWP/γ-Al ₂ O ₃ -USY	Yields based on feedstock, %: gasoline fraction up to 30, diesel fraction up to 62; sulfur and nitrogen content of the products up to 50 and 20 ppm, respectively; cetane number of diesel fraction up to 58	[146]
Brown coal pyrolysis tar	300°C, 8 MPa, pressure vessel; reaction time: until the pressure ceases to decrease	CoMo/Al ₂ O ₃ (BASF 0852)	Yield of S.B.–400°C fraction up to 40%, yield of residue ~15%; remainder: aqueous phase	[161, 162]
Brown coal semicoking tar	450°C, 13.8 MPa	NiMo/Al ₂ O ₃ (BASF M8-20) CoMo/Al ₂ O ₃ (ICI-71-1)	Degree of deoxygenation up to 95%, content of aromatic hydrocarbons in the product up to 56%, product density 851–871 kg m ⁻³ On CoMo/Al ₂ O ₃ catalyst, compared to NiMo/Al ₂ O ₃ catalyst, product with slightly higher content of aromatic hydrocarbons was obtained	[163]
214–510°C fraction of semicoking tar	390°C, 14 MPa, 0.5 h ⁻¹ , H ₂ /feed 1600 L _{n,c} L ⁻¹	NiMo/Al ₂ O ₃	Product contains 155 ppm nitrogen (degree of denitrogenation 99%) and 23 ppm sulfur (degree of desulfurization 99%); density 885 kg m ⁻³ ; yield, %: gasoline fraction 14 and diesel fraction 63	[164]

Table 9 (Contd.)

Feedstock	Optimum process conditions	Catalyst	Result	References
Coal liquefaction distillate	400°C, 14 MPa, 1 h, pressure vessel	FeOOH (unsupported) NiMo/Al ₂ O ₃	Total conversion of asphaltenes, preasphaltenes, and THF-insoluble compounds 28% on FeOOH and 71% on NiMo/Al ₂ O ₃	[165]
S.B.-360°C fraction of medium-temperature coking tar	Hydrofining: 360°C, 6 MPa, 0.4 h ⁻¹ , H ₂ /feed 1600 L _{n.c.} L ⁻¹ Hydrocracking: 380°C, 6 MPa, 0.4 h ⁻¹ , H ₂ /feed 1600 L _{n.c.} L ⁻¹	Hydrofining: CoMo/γ-Al ₂ O ₃ Hydrocracking: NiW/γ-Al ₂ O ₃	Yield, % gasoline fraction 20 and diesel fraction 77; content, ppm, based on feedstock: sulfur in gasoline fraction 71, sulfur in diesel fraction 54, nitrogen 14 and 8, respectively	[166]
Benzene, naphthalene, triphenylmethane, 9-phenylanthracene, 1-methoxynaphthalene, benzyloxybenzene, oxybis(methylene) dibenzene (OBMDB)	100–170°C, 4 MPa, 2 h, pressure vessel	Ni/MFA (microfibrinous attapulgite)	Conversion, %: benzene 49, OBMDB 62, benzyloxybenzene 78, triphenylmethane 65, phenylanthracene 42	[167]
Coal pyrolysis tar	Without hydrogen, fining of pyrolysis products at reactor outlet, 600°C	Co/C, Ni/C, Cu/C, Zn/C, where C is carbon obtained from pyrolysis	Degree of desulfurization, denitrogenation, and deoxygenation 37, 46, and 3%, respectively; the best results were obtained on Co/C, Ni/C, and Zn/C	[168]
1 : 1 mixture of coal coking tar and LGCC	375°C, 6.8 MPa, pressure vessel	NiMo/Al ₂ O ₃ , NiMoP/Al ₂ O ₃	On NiMoP/Al ₂ O ₃ catalyst, compared to NiMo/Al ₂ O ₃ catalyst, lower nitrogen and sulfur content of the product (N, 0.03 and 0.12%; S, 0.021 and 0.04%, respectively) and higher H : C ratio (1.69 and 1.56, respectively)	[169]
Coal gasification tar	390°C, 13.6 MPa, pressure vessel	NiW/Al ₂ O ₃ (Shell NT 550), NiW/SiO ₂ (Katalco 660)	Degree of desulfurization 100%, degree of denitrogenation 85% on NiW/Al ₂ O ₃ catalyst and 48% on NiW/SiO ₂ catalyst; the former catalyst ensured lower content of aromatic hydrocarbons	[170]

characteristics: fractional composition, content of asphaltenes and heteroatomic compounds, and coke residue; the possibility and economic feasibility of obtaining not only target products but also by-products (highly aromatic gasoline fraction, monocyclic aromatic hydrocarbons, phenols, pitch, etc.) are also taken into account. As a rule, one-step deep hydrotreating is insufficient to ensure for kerosene and diesel distillates the quality level prescribed by regulation documents: The products have increased density, insufficient cetane number, and insufficient height of sootless flame because of low PCA conversion [172]. Therefore, more and more authors suggest two- and three-step processing [126, 130, 133, 166], which can be implemented in one reactor with several beds of different catalysts or in two or three reactors. Hydrofining of the feedstock is performed in the first step, and hydrogenation and/or hydrocracking, in the second/third steps [153, 171, 172]. Such approach ensures higher flexibility with respect to the feedstock composition and the possibility of varying the assortment and relative yields of the products by varying the hydrocracking conditions; it expands the possibilities for choosing a second-step catalyst, because catalytic poisons are removed from the feedstock [34, 167].

Theoretically, refining of highly aromatic distillates in the step of their preparation to processing can be performed without using hydrogenation processes. The possibilities of extraction with acids and alkalis, adsorption treatment using clay minerals, coking [173], and extraction of phenols with an alkaline solution [174] have been examined. Extraction with acids and alkalis can ensure the removal of only 50% of nitrogen- and sulfur-containing compounds and virtually complete removal of phenols. This will certainly decrease the catalyst deactivation rate and the hydrogen consumption in the course of subsequent hydroprocessing; however, the yield of the target product will decrease also, because the raffinate yield is as low as 62–84% [173]. The same is true for the adsorption treatment. Furthermore, there are environmental problems with utilization of spent adsorbents and absorbents. Therefore, the above processes can hardly be considered as alternative to hydrogenation processes. Coking reduces the content of asphaltenes and highly condensed PCAs in the feedstock and therefore could be considered as a feedstock refining step; however, low distillate yield (50–60%) also restricts its use as an independent

process of feedstock pretreatment. Below we consider the flowsheets for processing of various kinds of highly aromatic feedstock in accordance with their specific features, and also combined flowsheets for processing of petroleum- and coal-derived feedstock.

As already noted, the presence of olefins and dienes in pyrolysis tar makes it necessary to perform preliminary hydrofining at a moderate temperature, sufficient for their saturation but insufficient for the polymerization to occur. Korosi and Rubin [157] suggest that the pyrolysis tar hydrofining be performed at a temperature of 170°C, a pressure of 5 MPa, and a space velocity of 1 h⁻¹ on Pd/Al₂O₃ catalyst. Milder conditions (135°C, 0.5 MPa) are suggested in [175], where a nickel catalyst is used. As a result, the degree of desulfurization reached 72%, the nitrogen content of the product was decreased to 16 ppm, and almost no hydrogenation of aromatic hydrocarbons was observed. Although changes in the nickel catalyst activity in the course of operation were not evaluated in [175], its rapid deactivation with sulfur compounds can be assumed. In the second step, hydrogenation on NiW or NiMo sulfide catalysts is performed in a separate reactor with several catalyst beds and intermediate feeding of a cold hydrogen-containing gas (HCG). Favorable fractional composition of pyrolysis tar (boiling interval 150–370°C [175]) and the absence of high-boiling residue make the hydrocracking installation unnecessary.

In contrast to pyrolysis tar having relatively narrow fractional composition, coal liquefaction, coking, and pyrolysis distillates are characterized by a large amount of the vacuum residue, giving rise to problems with implementation of hydrogenation processes, in particular, because of coking of the catalyst and heat-exchange apparatus and large hydrogen consumption. The problem can be solved by separation of the vacuum residue, followed by its gasification and Fischer–Tropsch synthesis of paraffin components of fuels from the syngas. Thus, coal distillates are a valuable feedstock because of the possibility of producing fuels of different hydrocarbon compositions: isoparaffin, naphthene, and naphthenoaromatic. The latter product is of interest as a hydrogen-donor additive to jet fuels, enhancing their thermal stability [176, 177].

Extensive data on various procedures for processing coal gasification tar to obtain jet fuel, including the results of pilot tests, are given in one of reports [178] of the series concerning production of jet fuels from

distillates of coal origin. Four flowsheets differing in the number of steps were considered. The first step is the simplest. It involves hydrofining in an expanded catalyst bed and hydrocracking of the residue to increase the operation life of the kerosene fraction. Because the feedstock is not fractionated prior to feeding into the hydrofining reactor, the equipment volume and HCG are utilized inefficiently, as the feedstock contains the fraction boiling in the interval up to 150°C, which cannot be included into the jet fuel formulation. This problem was solved in construction of the second flowsheet: The second hydrofining step was additionally introduced to decrease the content of nitrogen and aromatic hydrocarbons in the product. Introduction of the hydrocracking installation into the flowsheet allows the target product yield to be increased owing to an increase in the conversion of the residue. The most complex flowsheet involves hydrofining in the expanded catalyst bed to remove nitrogen-containing compounds and olefins and to partially hydrogenate PCAs, which allows the subsequent fractionation to be performed without significant coking on the apparatus walls. The second step of hydrofining in a fixed catalyst bed is aimed at further denitrogenation and hydrogenation of aromatic hydrocarbons. The nitrogen content of the hydrocracking feed does not exceed 10 ppm. The NiMo/Al₂O₃ catalyst is used in the first step, and the NiWP/Al₂O₃ catalyst, in the second step; the hydrocracking reactor is charged with the NiW/Y catalyst. The operation conditions are as follows: first and second hydrofining reactors, 400°C, 13.6 MPa, 1 h⁻¹; hydrocracking reactor: 355°C, 10.8 MPa, 0.7 h⁻¹. The product is treated with a clay adsorbent to remove resins.

Patent [179] suggests that hydrofining be performed in one reactor containing two catalyst beds: for hydrodemetalation and hydrodesulfurization. The use of the Pd- or Pt-containing catalyst in the hydrogenation step allows the PCA hydrogenation to be performed at a moderate temperature (225–260°C) and a pressure of 6.8 MPa [180]; however, in this case the mixture fed to the hydrogenation reactor should contain no more than 20 ppm sulfur and 5 ppm nitrogen.

The use of reactors with fluidized catalyst bed for hydroprocessing of coal tar [181] allows the pressure differential, local catalyst overheating, and hence excessive catalyst coking to be avoided; it also simplifies removal of the spent catalyst from the system and its partial replacement with a fresh catalyst. The authors of

[57] suggest the LC-Fining hydrocracking process in a fluidized bed of the NiMo catalyst for hydroconversion of the >300°C residue. The process conditions are as follows: reactor temperature 415°C, pressure 13.6 MPa, and space velocity 1.5 h⁻¹; under these conditions, the yield of the fraction boiling up to 300°C is 69–77%, the degree of denitrogenation is about 80%, and the degree of desulfurization exceeds 90%. The further processing of the hydrocracking products involves hydrodenitrogenation of the fraction boiling up to 480°C in a reactor with a fixed catalyst bed, selective hydrocracking in a reactor with a fixed bed of a zeolite-containing catalyst, fractionation with the recovery of the 140–305°C fraction, and its final purification by adsorption treatment with bentonite.

An important advantage of reactors with a fluidized catalyst bed, as well of slurry reactors, is no pressure and temperature differential in the catalyst bed. This is extremely important, because hydrogenation of aromatic hydrocarbon concentrates occurs with a large heat release, and it is even suggested [182] that straight-run gas oil be introduced into the highly aromatic feedstock to decrease the thermal effect of the reaction and simplify the temperature control in hydrogenation performed in reactors with a fixed catalyst bed.

In production of jet fuel from highly aromatic feedstock, separate hydrogenation of close-cut 30-deg fractions of the feedstock, followed by compounding of the hydrogenation products, is suggested for solving the problem of competition for active sites in multicomponent mixtures [183].

Production of fuels from oil shale pyrolysis products has certain specific features associated with very high nitrogen content (1.5–2%), presence of metals, arsenic, mechanical impurities, olefins, and dienes, and relatively high content of *n*-paraffins in comparison with other kinds of highly aromatic feedstock [184–186]. This should be taken into account in designing flowsheets for processing of such feedstock. The flowsheets for processing of shale pyrolysis products include blocks for adsorption and extraction treatment of the feedstock or products [184–186]. In the first case, a spent catalyst, clay mineral, etc., can be used as an adsorbent; the process can be performed at temperatures of up to 260°C for the hydrogenation of olefins and dienes. In the second case, basic nitrogen-containing compounds are extracted with an acid (sulfuric, phosphoric) [186] or with a polar solvent.

Along with the production of jet and diesel fuels, coal-derived distillates are of interest as a feedstock for producing monocyclic aromatic hydrocarbons, phenols, coke, and other products [129, 187]. The flowsheet provides for hydrocracking, coking, and catalytic cracking, which expands the potential of fuel fractions; however, these processes are economically appropriate only at high productive capacity of the plant. If liquid products of coal coking and gasification are not available in sufficient amount, their processing can be integrated with traditional oil refining processes. This approach, suggested in [140, 151, 175, 188], opens wide possibilities of combining the feedstock with the aim of optimizing its composition from the viewpoint of characteristics of the fuels obtained. Specifically this approach was suggested at the Pennsylvania State University (the United States) for obtaining jet fuel from coal tar and LGCC [115]. Both distillates (joint hydrofining of catalytic cracking gas oil and pyrolysis tar [175] or distillates of coal origin [140, 151]) and coal itself (joint decelerated coking of coal, petroleum tar, and heavy gas oil from catalytic cracking [140, 151, 188]) can be involved in processing. The flowsheets for joint processing of petroleum and coal feedstock are described in detail in [188] and are not presented here; only the most important aspects of processing of mixed feedstock will be briefly considered.

Flowsheets for joint hydroprocessing of LGCC (180–410°C) and coal tar (170–480°C), differing in the arrangement of the fractionation columns (before and after the feedstock hydrofining block), are considered in [140]. In the first case, separation of the >300°C residue prevents the catalyst coking and deactivation, but the yield of the target product, jet fuel, decreases in this case. After hydrofining, the product is subjected to hydrodearomatization. The mixed feedstock, compared to coal tar, is characterized by higher H : C ratio and lower content of heteroatoms, which undoubtedly simplifies its hydroprocessing. Similarly, pyrolysis tar compared to LGCC is characterized by lower nitrogen and sulfur content [175], but hydrogenation of olefins and dienes is required before introducing it into the feedstock.

To complete this section, we should mention several nontraditional methods for processing highly aromatic distillates, such as adsorption desulfurization on alumina, activated carbon, or zeolite adsorbents [140], extraction of coal with highly aromatic gas oil fractions with the aim of subsequent hydrogenation of the mixed

feedstock obtained [188], and oxidative desulfurization of coal distillates [189]. An interesting way to boost the cetane number of an aromatic diesel fraction obtained from coal is suggested in a patent [190]. Aromatic hydrocarbons are alkylated with olefins (e.g., 1-heptene) on ion-exchange resins or zeolites with the subsequent hydrogenation of alkylaromatic hydrocarbons. As a result, the cetane number increases by ~4 units only in the alkylation step. Similarly, alkylation of aromatic hydrocarbons with olefins, followed by hydrogenation of the alkylate, was suggested [191] for producing a component of jet fuels.

The above analysis of possibilities of producing fuels from highly aromatic wastes shows that the fractional composition and the content of heteroatoms, asphaltenes, olefins, and dienes is taken into account when choosing the feedstock and process configuration, but little attention is paid to the hydrocarbon composition of the feedstock and to the mutual influence of hydrocarbons in hydrogenation processes. In addition, it is interesting to determine how the feedstock composition and extent of its conversion in hydrogenation and hydrocracking influence the physicochemical and operation characteristics of fuels obtained. This problem is discussed in a separate review [192].

CONCLUSIONS

This review summarizes the data on the use of highly aromatic wastes in production of high-density low-congealing fuels with unique properties. Numerous studies in this field confirm that it shows much promise. The urgency of further studies of processes for producing high-density naphthene aviation and diesel fuels and of optimization of the feedstock composition for their production is beyond doubt. Only such kinds of feedstock are suitable for producing fuels for supersonic aviation, meeting the set of requirements to the stability, energetic parameters, and low-temperature characteristics. Therefore, the development of new catalysts and procedures for hydrogenation processing of highly aromatic fractions is required. Also, it becomes necessary to develop modern approaches to studying the composition of fuels produced from nontraditional feedstock with the aim of both process optimization and evaluation of possibilities for controlling the operation properties of specialty fuels on the basis of structure–property diagrams.

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