

# Physicochemical Properties and Performance Characteristics of Naphthenoaromatic Jet and Diesel Fuels Obtained by Hydrotreating of Highly Aromatic Fractions

N. N. Petrukhina<sup>a, \*</sup> and A. A. Maksimov<sup>a, b</sup>

<sup>a</sup>*Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia*

<sup>b</sup>*Faculty of Chemistry, Moscow State University, Moscow, Russia*

\**e-mail: n.petrukhina@ips.ac.ru*

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**Abstract**—The composition and physicochemical and chemotological properties of jet and diesel fuels obtained by hydrogen treatment of highly aromatic fractions—light cycle oil, pyrolysis tar, and coal tar—are considered in comparison with fuels obtained by hydrotreating of straight-run petroleum fractions. The influence of the hydrocarbon composition on the density, calorific value, viscosity, pour point, smoke point, cetane number, compatibility with elastomers, sooting tendency, combustion stability, and CO and NO<sub>x</sub> emissions of fuels are also considered. The interrelation of the composition of hydrocarbons and heteroatomic compounds of naphthenic jet fuels with thermo-oxidative and thermal stability has been analyzed in detail, and differences between the fuels in stability depending on the feedstock and hydrogenation depth have been shown. The usefulness of naphthenoaromatic distillates as additives that enhance both the thermal and thermo-oxidative stability of petroleum jet fuels is pointed out. Promising fields of research have been defined, including selective hydrogenation to produce certain stereoisomers; a targeted approach to feedstock compounding; and optimization of fuel composition to obtain desired characteristics using modern analytical techniques, such as GC × GC, HPLC, GC–MS, GC/TOF–MS, and ESI–MS.

**Keywords:** thermally stable jet fuel, high-density jet fuel, naphthenic fuel, thermo-oxidative stability, calorific value, coal tar

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The production of high-density aviation fuels with a high volumetric calorific value and thermal-oxidative stability is a strategic task, which is extremely important for the development of unmanned and military aviation. Thermo-oxidative stability is one of the main characteristics of fuels intended for supersonic aircrafts, since the fuel, in addition to combustion in the engine, is used to cool aircraft structure parts that experience kinetic heating due to the friction of high-velocity incoming air. Furthermore, the improvement of aviation gas turbine engines is accompanied by an increase in air and gas temperature along the engine path, i.e., by growth of its heat release rate and, hence, an increasing heat release into the fuel [1]. Thus, at a flight speed of 3M, the fuel can be heated to a temperature of 350°C and higher, which inevitably entails thermal degradation of paraffin hydrocarbons and will accelerate the coking and dehydrogenation processes [2]. In addition to enhancing the thermo-oxidative stability of jet fuels for supersonic aircraft, studies are underway to develop endothermic fuels that provide additional heat pickup through endothermic reactions, for example dehydrogenation [2]. The most

important properties of aviation fuels that influence the prospects for their use are the calorific value and density, which determine fuel consumption and possible on-board reserves and, as a consequence, the range of flight.

High-density thermostable aviation and rocket fuels with a density of more than 700 kg/cm<sup>3</sup> (see below) are individual hydrocarbons containing several strained naphthenic cycles and obtained, in particular, by oligomerization of cyclopentadiene [3–6] or pinene [7] and isomerization of either tricyclic naphthenes into diamond-like hydrocarbons [8, 9] or a mixture of naphthenic hydrocarbons obtained by hydrogenation of concentrates of aromatic compounds [10]. Highly aromatic refinery and coke chemistry wastes (cycle oils, cracker gas oils, coal tar, liquid pyrolysis products) have a huge potential as feedstock for the production of thermally stable jet fuel and low-pour-point diesel fuel. This area of research is of current importance not only from the viewpoint of the possibility of obtaining specialty fuels [1, 2], but also from the perspective of diversification of raw materials for manufacturing conventional aviation and diesel

fuels and development of scientific bases and technologies for alternative aviation fuel [11–15].

The technological foundations for the production of naphthenoaromatic fuels and their performance characteristics have been studied in most detail in the United States. High-density thermostable fuel JP-900 (JP-8C) was obtained from a mixture of coal gasifying and coking tars and light cycle oil. In addition to the lower cost in comparison with individual naphthenic hydrocarbons [16], the resulting fuel in accordance with its hydrocarbon composition is characterized by unique properties, primarily, such as a high density, thermal and thermo-oxidative stability, and excellent low-temperature properties. In Russia, thermally stable, high density T-6 and T-8V fuels obtained by hydrotreating of highly aromatic and straight-run distillates or distillation of naphthenic oils are known.

In this review, we have attempted to summarize information on the particular composition, performance characteristics, and chemotological and environmental properties of jet and diesel fuels derived from highly aromatic wastes of various origins.

#### COMPOSITION, PHYSICOCHEMICAL PROPERTIES, AND PERFORMANCE CHARACTERISTICS OF NAPHTHENIC JET FUELS

Of the main jet fuel characteristics regulated by the normative documents GOST 10227-86 and GOST 52050-2006, density, aromatics and sulfur contents, cold-flow properties, lower calorific value, smoke point, and thermo-oxidative stability are directly determined by the hydrocarbon composition. The composition of the fuel and some of its characteristics affect chemotological properties, such as emissions of particulate matter and nitrogen oxides, compatibility with fuel system rubber products, combustion efficiency, and combustion characteristics [17, 18]. The other characteristics—fractional composition, flash point, water content, specific electrical conductivity, etc.—are related to a significantly lesser extent to the feedstock from which fuel is produced and will not be considered in this review.

Naphthenic jet fuels can be obtained from kerosene fractions of naphthenic oils (straight-run fuels) or by hydrotreating of highly aromatic feedstock (cycle oils, coker gas oils, pyrolysis tars, coal tar, and their mixtures). The technologies for manufacturing fuels from high-aromatic distillates will be considered in more detail in the forthcoming paper in continuation of this review.

The composition of jet fuels produced from high-aromatic distillates by hydrotreating differs fundamentally from that of the fuels manufactured by hydrotreating straight-run feedstock and from Fischer–Tropsch<sup>1</sup> synthesis products: due to the pre-

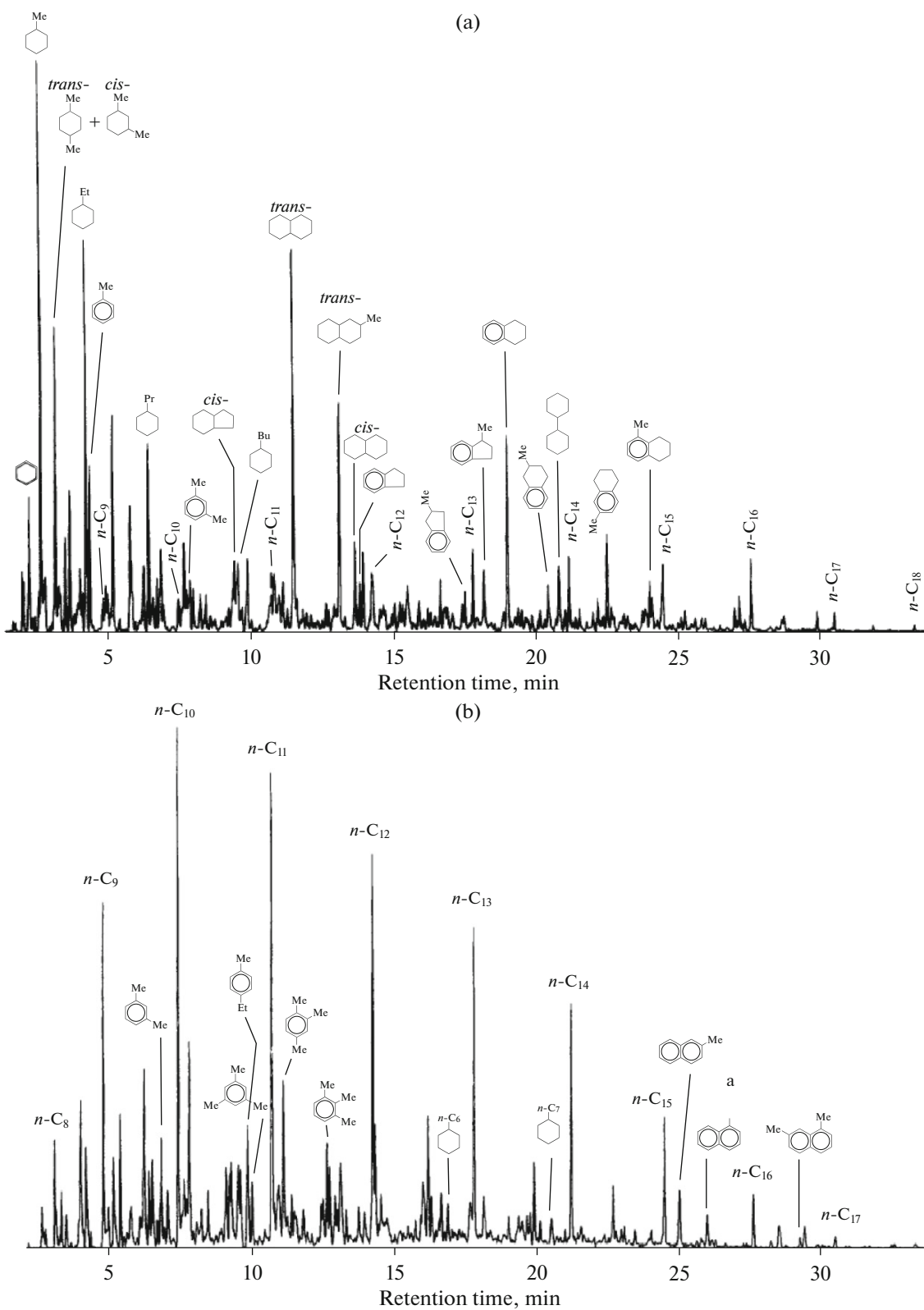
dominance of naphthenic and naphthenoaromatic hydrocarbons, the former fuels are characterized by higher density, volumetric calorific value, and thermo-oxidative and thermal stability and by excellent low-temperature properties [16, 19–23]. The main components of the fuel obtained from highly aromatic distillates are *cis*- and *trans*-decalins, tetralin, their methyl- and dimethylsubstituted derivatives, *cis*- and *trans*-octahydroindene, alkylcyclohexanes, perhydrophenylene, tetrahydroanthracene, perhydrofluorene, perhydroanthracene, and bicyclohexyl (see Fig. 1) [16, 20, 21], whereas petroleum-based jet fuel, for example JP-8, consists mainly of *n*-alkanes and alkylaromatic hydrocarbons. Table 1 collates characteristics of the hydrocarbon-group composition (determined by the GC–MS method according to ASTM D2425) of fuel obtained from coal distillates, petroleum fuel JP-8, and Fischer–Tropsch synthetic fuel [22]. As can be seen, the fuel obtained by the hydrogen treatment of the highly aromatic feedstock almost does not contain paraffins, whereas the petroleum-based or the synthetic fuel consist of hydrocarbons of this class by more than half or almost completely, respectively.

The nitrogen and sulfur contents and concentrations of naphthalenes, tetralins, and decalin obviously depend on the degree of hydrogenation of the product and, as shown in [24], affects the stability of the fuel. In addition to the hydrogenation depth, the fuel composition depends on the prevalence of certain hydrocarbon classes: naphthenic, alkylaromatic, unsubstituted aromatic, etc., in the feedstock. Table 2 shows the hydrocarbon-group composition and proton group contents according to <sup>1</sup>H NMR data for the components of JP-900 fuel: hydrogenated light cycle oil (LCO), hydrogenated fraction of coal tar, and their 1 : 1 (v/v) mixture [25]. For comparison, data for the petroleum fuel JP-8 are given. The LCO hydrogenation product is characterized by a higher concentration of aliphatic hydrocarbons and cyclohexanes in comparison with the hydrogenated tar fraction.

Table 3 collates the characteristics of the JP-900 fuel sample obtained by hydrotreating a 1 : 1 mixture of LCO and coal tar [16], those for the fuel JP-8, the standards for Russian fuels T-6 and T-8V, and characteristics of the fuel obtained from a coal liquefaction distillate at the Institute of Fossil Fuels (IGI) [1]. In the notation of the fuel brand JP-900, the figure 900 refers to the maximum temperature (900°F = 482°C) of fuel operation. As can be seen, the fuels T-6 and T-8V are superior to JP-900 in calorific value and the IGI fuel derived from coal is much superior to the foreign analogue, but is inferior to it in density. The fuel T-6 has a heavier fractional composition compared to JP-900.

In general, jet fuels derived from highly aromatic coal and shale distillates may contain up to 25 vol % aromatic hydrocarbons, 0–80 ppm of nitrogen, up to

<sup>1</sup> Hereinafter, the isomerization products of Fischer–Tropsch waxes are meant.



**Fig. 1.** Total ion current mass chromatograms of (a) jet fuel obtained by hydrotreating coal distillates and (b) petroleum-based jet fuel JP-8 [20].

**Table 1.** Hydrocarbon-group composition of JP-900 fuel [16, 22]

Hydrocarbon group	Content in jet fuel, vol %		
	naphthenic, as obtained from coal distillates	petroleum JP-8	obtained by Fischer–Tropsch synthesis
Paraffins	0.6	57.2	99.3
Naphthenes:			
monocyclic	46.0	17.4	<0.2
bicyclic	46.7	6.1	0.7
tricyclic	4.6	0.6	<0.2
Alkylbenzenes	0.5	13.5	<0.2
Tetalins and indans	1.6	3.4	<0.2
Indenes $C_nH_{2n-10}$	<0.2	<0.2	<0.2
Naphthalene	<0.2	<0.2	<0.2
Alkyl-naphthalenes	<0.2	1.7	<0.2
Acenaphthenes	<0.2	<0.2	<0.2
Acenaphthylenes	<0.2	<0.2	<0.2
Tricyclic aromatics	<0.2	<0.2	<0.2

**Table 2.** Composition of the components of fuel JP-900: hydrogenated LCO, hydrogenated coal tar fraction, and their 1 : 1 (v/v) mixture [25]

Parameter	Hydrogenated LCO	Hydrogenated coal tar fraction	1 : 1 (v/v) blend	JP-8
Hydrocarbon group composition, %:				
Aliphatic hydrocarbons	38.0	2.2	22.9	86.9
Cyclohexanes	25.9	13.1	17.0	6.9
Alkylbenzenes, including tetralins	0	0	0	6.1
Indenes	0.8	3.3	1.0	0
Naphthalenes	0	0	0	0.2
Decalins	33.3	66.7	50.2	0
Tricyclic naphthenes	2.0	14.6	8.9	0
Proton content, %:				
in methyl groups in $\gamma$ - and $\delta$ -position to aromatic ring; in methyl groups in alkanes and cycloalkanes (0.5–1 ppm)	37.0	21.6	29.4	1.2
in $CH_2$ groups (1–1.4 ppm)	36.6	31.9	34.3	37.3
in the CH and $CH_2$ groups of alkanes and cycloalkanes, and also in the $\beta$ -position to the aromatic ring (1.4–2.05 ppm)	25.5	45.5	35.3	51.5
in $CH_3$ groups in the $\alpha$ -position to the aromatic ring (2.05–2.45 ppm)	0.7	0.7	0.7	2.6
in $CH_2$ groups in the $\alpha$ -position to the aromatic ring (2.45–3.0 ppm)	0.1	0.2	0.2	5.0
Total aliphatic protons:	99.9	99.9	99.9	97.6
in aromatic rings (6.5–9.0 ppm)	0.1	0.1	0.01	2.4
Heteroatoms content, ppm:				
sulfur	1	1	1	616
nitrogen	0	0	0	2

**Table 3.** Characteristics of a JP-900 fuel sample in comparison with JP-8 fuel [16]

Property	Standard for fuel JP-8 according to MIL-DTL-83133E	Value for fuel JP-900	Standard for fuel T-6 according to GOST 12308-2013	Standard for fuel T-8V according to GOST 12308-2013	Value for fuel from coal (IGI) [1]
Acid number, mg KOH/g	Max 0.015	0	0.5	—	0.5
Volume (weight) fraction of aromatic hydrocarbons, %	Max 25.0	1.9	8	20	(6.2)
Weight fraction of mercaptan sulfur, wt %	Max 0.002	0	None	0.001	None
Total sulfur, wt %	Max 0.3	0	0.05	0.10	0.0003
Fractional composition, °C:					
IBP	Report	181	195	165	124
10 vol %	Max 205	192	220	185	n/d
20 vol %	Report	194	—	—	n/d
50 vol %	Report	204	225	Not regulated	n/d
90 vol %	Report	243	290	Not regulated	n/d
FBP	Max 300	270	315	280	220
Flash point, °C	Max 38	61	62	45	37
Pour (crystallization onset) point, °C	Not above -47	-65	-60	-60	Below -60
Kinematic viscosity at -20°C, cSt	Max 8.0	7.5	—	—	n/d
Lower calorific value, kJ/kg	Min 42798	42800	42900	42900	43290
Hydrogen content, wt %	Min 13.4	13.2	n/d	n/d	n/d
Smoke point, mm	Min 19.0	22.0	20	20	36
Amount of naphthalene hydrocarbons, wt %	Max 3.0	0	(0.5)	(2.0)	n/d
Thermo-oxidative stability at test temperature 260°C (275°C):					
tube deposit	Max 3	<1	(3)	(3)	n/d
filter pressure drop, mmHg	Max 25	0	25	25	n/d
Existent gum, mg/100 mL	Max 7.0	3.8	4	4	none
Density at 15°C (20°C), kg/m <sup>3</sup>	775–840	870.2	(840)	(800)	(785)

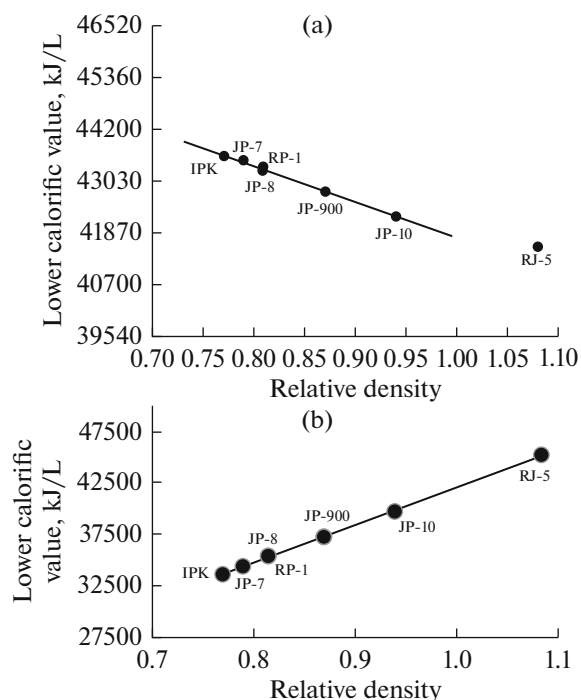
0.05 wt % sulfur, and 12.8–13.7 wt % hydrogen and, as a rule, have a pour point below -30°C and a calorific value in the range of 42 520–43 100 kJ/kg [26, 27]. The physicochemical properties and performance characteristics of jet fuels derived from highly aromatic distillates and their relation to the hydrocarbon composition are considered in detail below.

### Density

For hydrocarbons with the same number of carbon atoms in the molecule, the density increases in the order paraffins < naphthenes < aromatic hydrocarbons [28]. As the conversion of aromatic to naphthenic hydrocarbons increases, the density of fuel is markedly reduced. For comparison, the density of the kerosene fraction of coal tar is 970 kg/m<sup>3</sup> after hydro-

fining and 880 kg/m<sup>3</sup> after hydrogenation versus 890 and 840 kg/m<sup>3</sup>, respectively, for LCO after the same treatments [29].

As can be seen from Table 3, the density of JP-900 fuel is higher than that of JP-8, the difference being due to the predominance of naphthenic hydrocarbons in the former. The search for ways to increase the density of military jet fuels is caused by the limited volume of fuel tanks and inspired by the desire to increase the flight range and duration. Figure 2 shows the distribution of known brands of foreign jet fuels in density and calorific value [16]. Naphthenic fuel JP-900 in density and energy properties is only slightly inferior to the one-component specialty fuel JP-10, which is *exo*-tetrahydrodicyclopentadiene [5]. It is noteworthy that the feedstock resources for manufacturing the



**Fig. 2.** Correlation of (a) the specific and (b) the volumetric calorific value with the density of jet fuels: IPK stands for Fischer–Tropsch synthesis isoparaffins, JP-7 and RP-1 are the petroleum-based hydrocarbon fuels, JP-10 is *exo*-tetrahydrodicyclopentadiene; RJ-5 is a mixture of hexa- and pentacyclic isomers [5] [16].

fuel JP-10 are limited, and the cost of the fuel is incomparably greater than that of JP-900 [16]. Thus, fuels produced by the hydroprocessing of highly aromatic raw materials may well be considered as an alternative to specialty high-density fuels.

### Calorific Value

The calorific value of jet fuels increases linearly with the hydrogen weight fraction: for naphthoaromatic fuels derived from coal and shale distillates, from ~42500 kJ/kg for fuels with a hydrogen content of 13 wt % to ~43100 kJ/kg for those with a hydrogen content of 14 wt % [26, 27]. The calorific value of fuel almost linearly increases with the total content of alkanes and naphthenes [23], a decrease in the aromatics content from 25 to 5% increases the calorific value by 210 kJ/kg. For example, the calorific value of the hydrofined fraction of coal tar is 42470 kJ/kg and that of the hydrogenated product is 45217 kJ/kg [29].

The calorific value of *cis*-decalin is slightly higher than that of *trans*-decalin, being 42617 and 42535 kJ/kg, respectively [30]. The calorific value of alkyldecalins is higher than that of unsubstituted decalin, and it increases with the number of carbon atoms in the side chain to be 42659 kJ/kg for  $\alpha$ -methyldecalin, 42519 kJ/kg for  $\beta$ -methyldecalin, 42729 kJ/kg for

$\alpha$ -ethyldecalin, 42752 kJ/kg for  $\beta$ -ethyldecalin, 42845 kJ/kg for  $\alpha$ -isopropyldecalin, and 42891 kJ/kg for  $\alpha$ -*n*-butyldecalin [31].

A quantity of practical importance is volumetric calorific value, which should be above 36230 kJ/L for high-energy, high-density fuel. The volumetric calorific value of jet fuel obtained from kerosene fractions of crude oil is ~32280 kJ/L, and that of a mixture of decalin isomers is 37738 kJ/L [32]. Thus, from the point of view of energetic properties, decalins are desirable components of high-density fuels. In addition, decalin and tetralins are of interest as components of endothermic fuels [4], which are characterized by increased heat sink capability due to the occurrence of endothermic reactions, in particular dehydrogenation in the given case.

### Viscosity and Low-Temperature Properties

The viscosity of jet fuel at low temperatures largely determines its pumpability and atomization efficiency. The latter property, in turn, determines the intensity of coking in the combustion chamber, the combustion efficiency, and the possibility of fuel ignition during high-altitude engine start.

Rheological and low-temperature properties of fuels are determined by their hydrocarbon composition. Table 4 shows the viscosity values and pour points of some jet fuel hydrocarbons [23]. According to published data [26], the pour point and the viscosity of aromatic hydrocarbons almost linearly depend on the diameter of the molecule, which is determined by the number of rings and the length of the alkyl substituent. The pour point of naphthoaromatic fuel is largely determined by the molecular size of aromatic hydrocarbons, not their content. Probably, large aromatic molecules facilitates the ordering of nonaromatic molecules similarly to the formation of surfactant micelles. Typically, methyl-substituted aromatic hydrocarbons have a higher viscosity than the unsubstituted ones, but the viscosity of naphthenic hydrocarbons is not increased by introducing alkyl substituents.

Figure 3 shows viscosity–temperature curves for two petroleum jet fuels and JP-900 [16, 22, 33]. Due to a high concentration of *n*-paraffins, petroleum-based JP-8 fuel starts crystallizing at a temperature of (–52)–(–60)°C and forms a three-dimensional network of *n*-paraffins, which is evident from the sharp jump in dynamic viscosity. The JP-900 fuel “thickens”, its viscosity gradually increases with decreasing temperature, but conglomeration and crystal formation do not occur. Despite the lower pour point of JP-900 (–65°C) compared to jet fuel JP-8 (–50°C), the former has a higher viscosity at low temperatures (12.8 vs 7.9 cSt, respectively, at –40°C) [16, 22]. This difference in behavior of the fuels is analogous to the rheol-

ogy of high-paraffin and naphthenoaromatic crude oils and refinery products [34].

Returning to Table 4, it should be noted that the viscosity of *cis*- and *trans*-decalins is significantly higher in comparison with other hydrocarbons with the same number of carbon atoms. As a result, the viscosity increases on passing from the hydrofined fraction of coal tar or LCO to the hydrogenated products (by a factor of 1.40 or 1.13, respectively) [29]. In this connection, it was proposed [35] to reduce the viscosity of naphthenic fuels, which mainly contain decalins, by introducing 15–25% isoalkanes, for example, a hydrogenated propylene tetramer, whose viscosity is 4.2 times lower than the viscosity of the decalin concentrate at  $-34^{\circ}\text{C}$ .

Visual observations of the crystallization of fuels during low-temperature pumping showed that at a wall temperature of  $-70^{\circ}\text{C}$ , in contrast to petroleum jet fuel, JP-900 does not form a semisolid structure and the nascent crystals are smaller and do not cause pipeline clogging [22].

#### Smoke Point

The propensity of fuel to soot formation during combustion is characterized by smoke point. This is one of the indicators of quality of naphthenoaromatic fuels, a high value (22–28 mm) of which is provided only by deep hydrogenation. Thus, the smoke point is 8.2 mm for the hydrofined LCO fraction and 24.1 mm after hydrogenation [29]. Soot is a disordered polycyclic aromatic entity, the formation of which from paraffin molecules is preceded by the formation of hydrocarbon structures  $\text{C}_2\text{H}_2-$ ,  $\text{C}_2\text{H}_3-$ ,  $\text{C}_3\text{H}_3-$ , etc., which are then condensed into aromatic nuclei. The rate-determining step of the soot formation process is the formation of monocyclic aromatic hydrocarbons [36]. Aromatic molecules are the direct precursors of soot particles [37], and their presence in fuel significantly intensifies sooting [38, 39]. In this connection, the smoke point decreases with increasing aromatics content of the fuel and decreasing hydrogen content [26, 27, 40], but it increases with the concentration of naphthenes [23]. Moreover, as shown in [41], the dependence of the smoke point on the H/C ratio is polynomial for tricyclic hydrocarbons and linear for bicyclic ones.

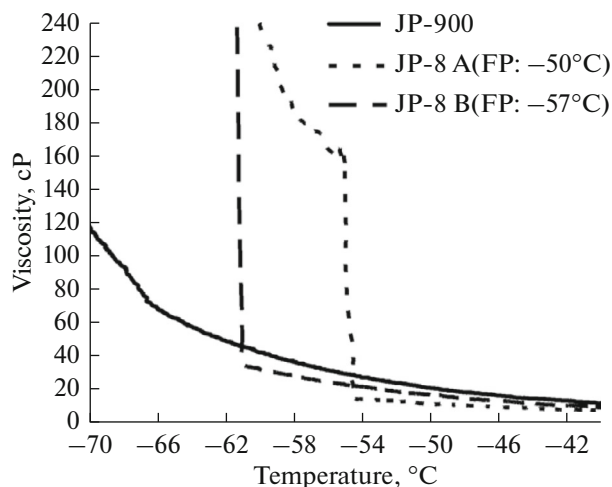
The introduction of decalins into fuel reduces soot formation; tricyclic naphthenes do not affect this characteristic; and the presence of naphthalene and phenanthrene, as expected, enhances sooting (Fig. 4) [41]. The addition of tricyclic naphthenes, on one hand, lowers the concentration of aromatic hydrocarbons in the fuel, thereby reducing the tendency to sooting; on the other hand, tricyclic naphthenes per se have a high propensity for soot formation.

Hydrogenation of bicyclic aromatic into naphthenoaromatic hydrocarbons reduces the fuel tendency to

**Table 4.** Viscosity and pour point of some jet fuel hydrocarbons [23]

Hydrocarbon	Kinematic viscosity, cSt, at a temperature of $38^{\circ}\text{C}$	Pour point, $^{\circ}\text{C}$
<i>n</i> -Octane	0.64	$-56.8$
Naphthalene	solid	80.3
Tetralin	1.66	$-35.8$
<i>cis</i> -Decalin	2.66	$-43.0$
<i>trans</i> -Decalin	1.82	$-30.5$
<i>n</i> -Decane	1.01	$-29.6$
<i>n</i> -Undecane	1.26	$-25.6$
<i>n</i> -Dodecane	1.54	$-9.6$

soot. Tetralin contains six aromatic carbon atoms in the molecule and is a potential precursor of soot particles. However, it is well known that naphthenoaromatic compounds act as hydrogen donors. The detachment of  $\text{H}^{\bullet}$  radicals and their participation in recombination reactions inhibit the combination of alkyl radicals and, hence, the condensation of polycyclic aromatic (PCA) hydrocarbons, thus increasing the thermal stability of the fuel and reducing the amount of carbon deposits at high temperatures [42]. As a result, such molecules are favorable for sooting inhibition, and the resulting negative effect of their addition to fuel is associated with their dehydrogenation to naphthalene, the precursor of soot particles [41]. The introduction of tetralin into fuel leads to greater sooting than the introduction of alkylbenzenes [43]. Decalins, in comparison with tetralin, show a less ability to transfer hydrogen, but additionally reduce soot formation because of a decrease in the concentration of aromatic hydrocarbons in the fuel.



**Fig. 3.** Viscosity–temperature curves of jet fuels JP-8 and JP-900 [16, 22, 33].

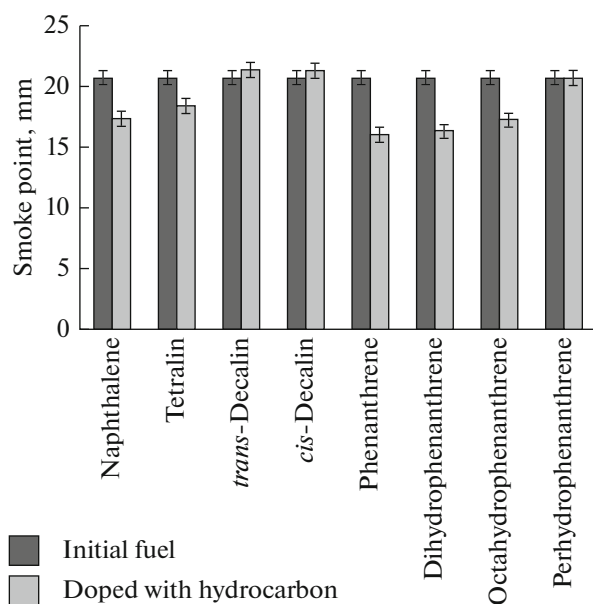


Fig. 4. Change in the smoke point of jet fuel by doping 5% hydrocarbons [41].

#### Emissions of Soot Particles, Hydrocarbons, Nitrogen Oxides, and Carbon Monoxide

Emissions of carbon monoxide, unburned hydrocarbons, and particulate matter increase with increasing thermo-oxidative stability of the fuel. Naphthenic and aromatic hydrocarbons are more stable to oxidation than alkanes [16, 23].

Figure 5 shows the dependence of the volume fraction of soot particles in the combustion gases of JP-8 and JP-900 fuels and Fischer–Tropsch distillate on the fuel–air equivalence ratio [37]. The emissions of particulate matter are insignificant at an equivalence ratio below 1.05, and they are higher for JP-8 than for JP-900 fuel, a difference that is due to the absence of aromatic hydrocarbons in the sample. Nevertheless, there are some reports [16–23, 33, 41] that the combustion of JP-900 fuel yields a greater amount of par-

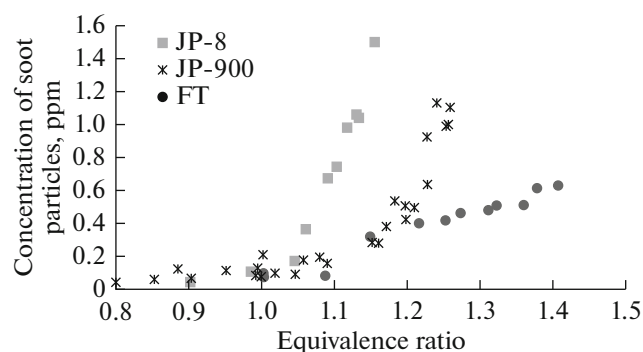


Fig. 5. Dependence of the concentration of soot particles in the combustion products of JP-8 and JP-900 fuels and the Fischer–Tropsch (FT) synthesis product [37] on the equivalence ratio.

ticulate matter than does a petroleum-based jet fuel. The JP-900 fuel is much more stable to oxidation and high temperatures, as follows from the very concept of its creation [44], and the dehydrogenation of naphthenes yielding PCA is one of the reasons for propensity of fuel JP-900 to soot. It was shown [45] that naphthenic high-density fuels T-6, Naphthyl, and JP-10 are characterized by a lower apparent burning rate, and in comparison with fuel TS-1, and a significantly (two times) higher activation energy of combustion at 300–550°C, which lead to an increase in emissions of CO and unburned hydrocarbons.

The results of comparative tests of JP-8 and JP-900 fuels in a T-63-A-700 turboshaft engine [16, 22] are of considerable interest (Table 5). The tests were carried out at ground<sup>2</sup> idle and normal rated power (cruise) conditions. The smoke of the exhaust, the concentration of solid particles on a quartz filter, and the particle concentration by the gravimetric method were determined. It can be seen that with the combustion of JP-900 fuel gives more solid particles at idle and differences at cruise are less noticeable. The particle size distribution for the two fuels is the same. In connection with increased soot formation and, accordingly, incomplete combustion of fuel, the mass consumption of fuel is increased by 3.5 and 5.1% to provide the same power at idle and cruise conditions, respectively.

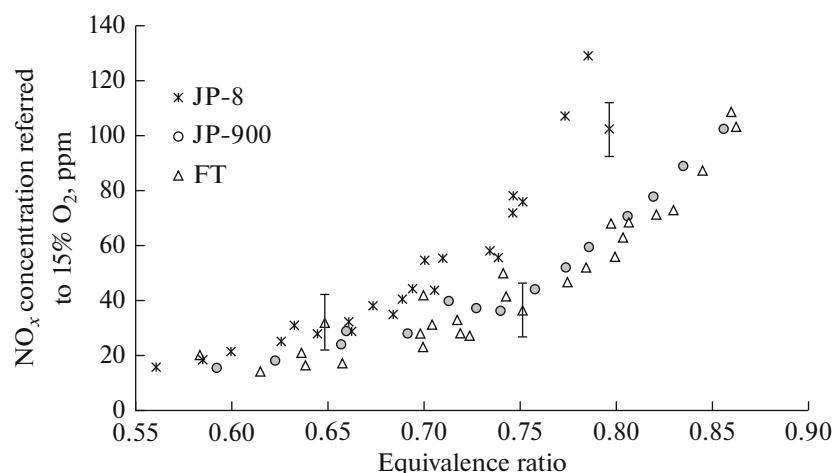
The CO emissions for JP-900 are higher by 21 and 18% at idle and cruise, respectively, in comparison with JP-8 [16, 22, 33]. However, according to other data [23, 37], the CO emissions from combustion of JP-900 are lower than those from JP-8; with an equivalence ratio below 0.8; JP-900 in this property approaches the synthetic isoparaffin fuel, which is characterized by the lowest carbon monoxide emission. Obviously, the differences in the results obtained

Table 5. Emissions of particulate matter in the testing of JP-8 and JP-900 fuels in a T-63-A-700 turboshaft engine [16, 22]

Fuel	Smoke	Particle concentration on quartz filter, mg/m <sup>3</sup>	Particle concentration by gravimetric method, mg/m <sup>3</sup>
Idle			
JP-8	7.3	5.7	3.0
JP-900	9.6	8.0	3.3
Normal rated power			
JP-8	37.0	9.2	10.5
JP-900	40.7	10.8	11.4

<sup>2</sup> The established engine operation at ground idle at the minimum speed of rotation and thrust, which ensure its stable operation and a given throttle response.





**Fig. 6.** Dependence of the concentration of nitrogen oxides in the combustion products of JP-8 and JP-900 fuels and FT product of the Fischer–Tropsch synthesis [37] on the equivalence ratio.

in different studies are due to the hydrocarbon composition of the selected JP-900 and JP-8 fuel samples. The composition of the latter can vary significantly depending on the crude oil from which the kerosene fraction was taken. The emissions of unburned hydrocarbons for JP-900 in comparison with JP-8 are greater by 30% at idle conditions and differ little at cruise [16, 22].

Figure 6 shows the dependences of  $\text{NO}_x$  emissions on the equivalence ratio for combustion of JP-900, JP-8, and isoparaffin fuel [37]. The concentration of nitrogen oxides in the combustion gases of JP-900 is lower than that in the combustion of JP-8, with  $\text{NO}_x$  emissions increasing sharply for the latter at an equivalence ratio of  $\Phi > 0.75$ , when the flame temperature reaches 1800 K, i.e., the Zeldovich high-temperature nitrogen oxidation mechanism is realized [46].

Despite the greater emission of CO, hydrocarbons, and particulate matter when using JP-900 fuel, the order of magnitude of these changes is small relative to the other tested fuels derived from coal distillates and containing up to 41% aromatic hydrocarbons [16]. It should be noted again that thermo-oxidative stability is inversely related to the fuel combustion efficiency. A compromise between these characteristics can be achieved, in particular, by compounding naphthenic fuels with isoparaffinic fuels produced by the Fischer–Tropsch synthesis [47].

#### Combustion Stability

Comparative tests of JP-8 and JP-900 fuels in a model gas turbine combustor [37] showed that the fuels burn stably; pressure fluctuations do not exceed 1%. Only single pressure fluctuations exceeding 2% were observed for both fuels with an equivalence ratio of  $\Phi = 0.7\text{--}0.8$ , but without a distinct tendency. The comparative tests of a JP-900-

fired FJ44-3 gas turbine engine with a total duration of 21 h did not reveal any deviation in the engine performance from the figures obtained in the case of using Jet-A fuel [48].

#### Swelling of Elastomers

The ability of fuel to increase the volume of elastomers is a necessary property, and it is used to seal the fuel system. This property of fuel depends on the size and polarity of its molecules and their ability to form donor hydrogen bonds and penetrate into the polymer structure and is determined mainly by the concentration of aromatic hydrocarbons and heteroatomic compounds.

Fischer–Tropsch paraffin fuels do not ensure elastomer swelling, thereby limiting the possibility of their use in existing fuel systems without the introduction of aromatic hydrocarbons into the fuel composition [49, 50]. Naphthenes, like aromatic hydrocarbons, ensure the swelling of rubbers.

The JP-900 fuel, which is almost free of aromatic hydrocarbons, is not inferior to JP-8 in ability to increase the volume of nitrile rubber O-rings (Fig. 7) [16, 22, 33]. This finding leads to the conclusion that naphthenic fuels can be used as additives for synthetic isoparaffin fuels to make them compliant with the latest requirements for elastomers.

#### THERMO-OXIDATIVE AND THERMAL STABILITY OF JET FUELS PRODUCED BY HYDROGENATION OF HIGHLY AROMATIC FEEDSTOCK

Since the urgency of developing naphthenic fuels is dictated not only by the desire to diversify sources of raw materials, but also the need to create thermally stable fuels for supersonic aircraft, a lot of work has

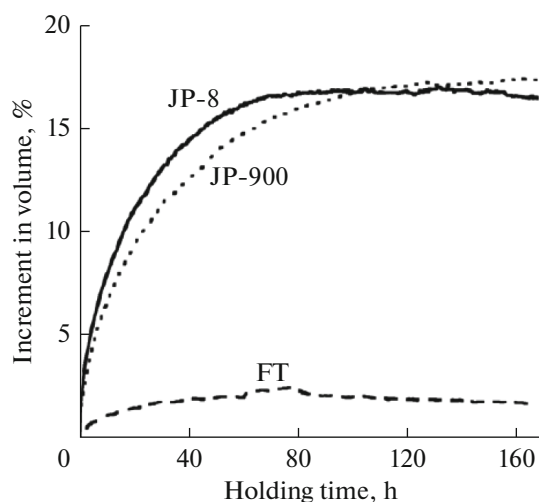


Fig. 7. Increment in the volume of nitrile rubber O-rings in JP-8 and JP-900 fuels and Fischer–Tropsch distillate (FT) at room temperature [16, 22, 33].

been devoted to this property of fuels [23, 33, 51–61]. The thermal stability of jet fuel determines the possibility of using them in supersonic flights to cool aircraft structure parts. In this regard, the thermo-oxidative and thermal stability of naphthenic jet fuels is placed in an independent section.

First of all, it is necessary to identify the types of thermal stability of jet fuels. Conditionally, it is possible to distinguish three temperature regions of oxidation and degradation of fuels: from room temperature

to 80, 80–290, and above 290–300°C. The first range corresponds to the oxidation of fuel during storage, the second refers to operation in the fuel system (thermo-oxidative stability), and the third characterizes very high flight speeds and differs from the first two by intense pyrolysis processes (thermal stability). These temperature ranges may be somewhat different [51], which is not of fundamental importance. The chemistry of the processes occurring in these temperature regions assumes their separate analysis.

#### Storage Stability of Jet Fuels

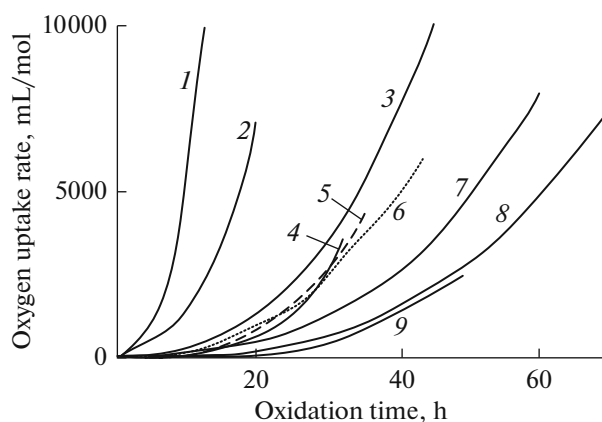
During fuel storage in air, oxidative processes leading to the formation of gum, particulates, and peroxides occur [52, 62]. Storage stability is determined in model experiments on accelerated oxidation of fuel under the influence of oxygen or air at a fixed temperature (ASTM D2274 and D4625) and quantitatively characterized by a peroxide value (corresponding to the peroxide content of the fuel and determined according to ASTM D3703) and existent gum content (ASTM D381).

A small number of studies have been devoted to the oxidation of naphthenic fuels during storage [52, 63]. In general, it is reported that hydrogenation fuels have low propensity to oxidation during storage [62] because of the absence of hetero compounds in them. Thus, it was shown [63] that fuels derived from highly aromatic coal distillate exhibit greater stability on storage for three weeks at 80°C under an oxygen pressure of 0.68 MPa (ASTM D2274 method) compared to JP-8 fuel. The higher stability is expressed in a smaller proportion of the sediment and a smaller color change, but the peroxide value of the fuel after storage is significantly higher than for JP-8. During the third or fourth week of storage, after reaching a

Table 6. Existent gum content and peroxide value after storage at 60°C for 4 weeks of shale-derived fuel with different nitrogen contents [52]\*

Nitrogen content, ppm	Existent gum, mg/100 mL	Peroxide value, mg/kg
Fuel nitrogen compounds not subjected to thermal degradation		
0	0	60
8.4	1.4	64.3
25.0	5.4	86.8
125.0	1.6	42.5
5-Ethyl-2-methylpyridine		
50	5.0	83.0
2,5-Dimethylpyrrole		
50	0.4	4.2

\* The existent gum before storage was 0 mg/100 mL in all cases; the peroxide value was not higher than 1.4 mg/kg.



**Fig. 8.** Kinetics of oxygen consumption in the oxidation of naphthenes and alkanes [65]: (1) 9,10-diisobutylperhydroanthracene, (2) perhydroanthracene, (3) octadecyldecalin, (4) amylocyclopentane, (5) bicyclohexyl, (6) decalin, (7) octadecylcyclohexane, (8) hexadecylcyclohexane, and (9) cetane.

maximum of the peroxide number, the intense formation of sediment and fuel darkening are observed. After four weeks of storage, the test fuel contains a 3.4 times greater amount of sediment and the peroxide value is 26 times that for JP-8.

One of the reasons for the formation of sediments in fuels is the presence of sulfur-, nitrogen- and oxygen-containing compounds, which interact with peroxides during fuel storage [52]. Condensation and dimerization of the free radicals formed leads to the formation of gum and precipitates. To a considerable extent, these processes are typical of fuels derived from shale distillates, which are characterized by high nitrogen content [64]. Acid extraction followed by adsorption purification, aimed at removing nitrogen-containing compounds from the fuel, increases the oxidation stability. Table 6 shows the existent gum content and the peroxide value of the fuel with different nitrogen contents after storage for 4 weeks at 60°C [52]. As can be seen, alkylpyridine and native nitrogen compounds of the fuel cause the most noticeable decrease in storage stability. The fact of accelerating oxidation and sedimentation in jet fuels by adding pyridine and quinoline is well known [51]. At the same time, indole and pyrrole almost do not affect the oxidation of fuels. The fuel oxidation mechanism will be discussed in detail in the next section.

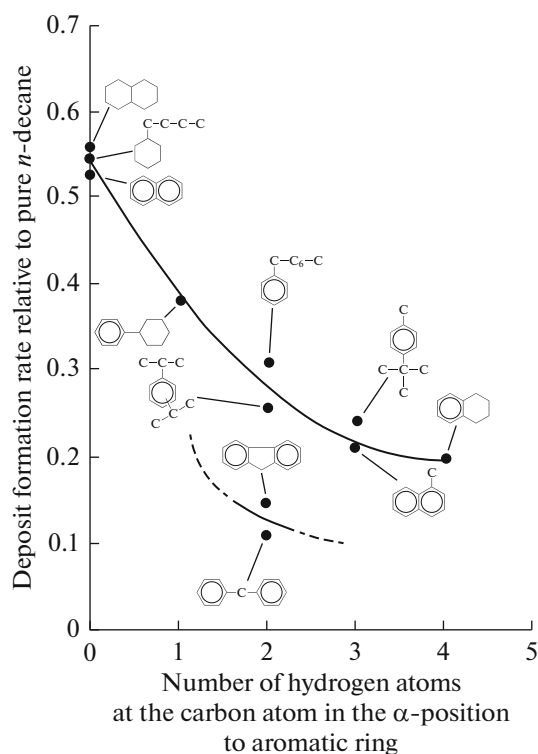
#### *Thermo-Oxidative Stability of Jet Fuels*

The oxidation of all hydrocarbons is characterized by the following general trends: the reactivity increases with the chain length, in the presence of double bonds, and in the presence of tertiary carbon atoms [65]. The rate of oxidation of unsubstituted aromatic hydrocarbons is lower than that of naphthenic hydrocarbons; an increase in the number of rings in the molecule of naphthenic hydrocarbons reduces their resistance to

oxidation because of a larger number of reactive tertiary carbon atoms. This conclusion is drawn on the basis of the close reactivity of decalin and dicyclohexane and higher reactivity of anthracene [65]. Figure 8 shows oxygen uptake curves for the case of oxidation of various naphthenes and paraffins at a temperature of 110°C. It is seen that tricyclic naphthenes are the most reactive. This fact was noted by Berkhouz [53] in relation to the thermo-oxidative stability of the hydrogenated coal tar fraction containing perhydroanthracene, perhydrophenanthrene, and perhydrofluorene.

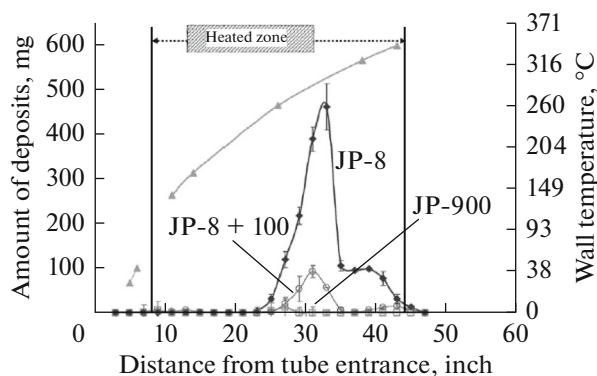
The presence of an alkyl chain in the molecule of naphthenic or aromatic hydrocarbons increases the reactivity. In this context, tetralin is considerably superior to naphthalene in reactivity. The increased propensity to oxidation of naphthenoaromatic hydrocarbons is due to the presence of four relatively weak C–H bonds in the  $\alpha$ -position to the benzene ring. The reaction proceeds with autoacceleration [66]. At a temperature of 50°C, the oxidation rate constant of tetralin is seven times that of cumene and only slightly lower than that of styrene [67].

In view of the foregoing, the differences in thermo-oxidative stability between the hydrodesulfurized and hydrogenated fractions become clear [54]. Since tetralin is readily oxidized at temperatures below 100°C [66], storage in air leads to buildup of hydroperoxides. For example, the hydrofined fraction of coal tar after storage with air access contains 212 ppm of peroxides, whereas the hydrogenated fraction contains only 7 ppm. It is evident that the presence of primary oxidation products in naphthenoaromatic fuels is responsible for their low thermo-oxidative stability under test conditions. Purging of such fuel with nitrogen does not improve its oxidation stability, in contrast to purging of naphthenic fuel [54]. Similarly, hydrogenated LCO contains more peroxides than the hydrogenated fraction of the coal tar (peroxide number is



**Fig. 9.** The rate of formation of carbonaceous deposits during the oxidation of a mixture of 90% *n*-decane and 10% aromatic hydrocarbon at a temperature of 120°C [70].

28.7 vs 1.8 ppm, respectively) [25] because of the presence of alkylaromatic hydrocarbons and alkylcyclohexanes in LCO, whereas the hydrogenated tar fraction contains mainly unsubstituted hydrocarbons. It was shown [68] that cymene and isopropylbenzene admixed to jet fuels reduces their oxidation stability.



**Fig. 10.** Profile of heater tube deposit in the pumping of JP-8, JP-8 + 100, and JP-900 fuels [16, 22, 33].

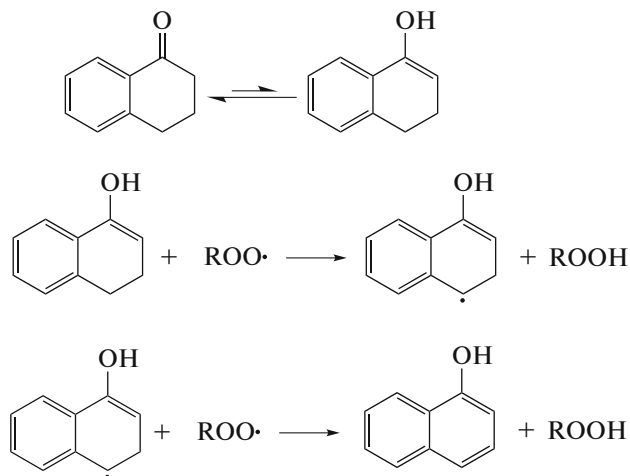
The reactivity of alkylbenzenes increases with the chain length and, to a lesser extent, in the presence of several chains with the same total number of carbon atoms. Among alkyl-naphthalenes,  $\alpha$ -alkyl-naphthalenes are more reactive, since the  $\alpha$ -carbon atom is activated by the conjugation of two rings. Similarly to alkylbenzenes, the reactivity increases greater with the number of carbon atoms in the side chain than with an increase in the number of substituents. The absence of a hydrogen atom at the carbon atom in the  $\alpha$ -position (*tert*-butyl-naphthalene) reduces the tendency to oxidation. The oxidation behavior of anthracene and phenanthrene derivatives is similar to that of naphthalene [65].

The high propensity of tetralin to oxidation can be responsible for low thermo-oxidative stability of the 165–185 and 185–215°C low-boiling fractions of jet fuel obtained by hydrotreating high-aromatic coal distillates, in comparison with high-boiling fractions [69]. These fractions have a high tetralin content, whereas high-boiling fractions contain mainly decalin. On the other hand, the differences may be due to uneven distribution of sulfides and sulfoxides (native oxidation inhibitors); i.e., to their preferential concentration in high-boiling fractions [62].

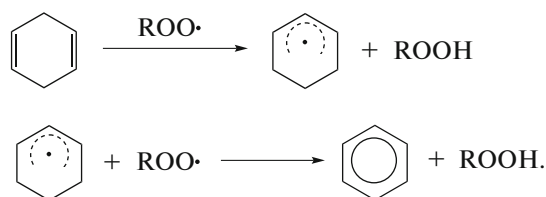
Tetralin, diphenylmethane, and alkylbenzenes inhibit the oxidation of other compounds, a property that is widely known in the combined oxidation of tetralin and cumene [67]. The tetralyl peroxide radical generated during the rapid oxidation of tetralin intensifies chain termination reactions and protects cumene from oxidation. A similar effect was observed for 1-methylnaphthalene–*n*-decane, 2-methylnaphthalene–*n*-decane, tetralin–*n*-decane, phenylcyclohexane–*n*-decane, etc. mixtures [70, 71]. The effectiveness of an inhibitor, like the activity of an alkylaromatic compound in the oxidation reaction, is proportional to the number of hydrogen atoms at the carbon atom in the  $\alpha$ -position to the aromatic ring (Fig. 9). In addition, the stability of the peroxide radical formed via the oxidation of the inhibitor is important. The ROO $\cdot$  radical formed by oxidation, for example, of tetralin is resonance-stabilized. The higher inhibitory efficiency of diphenylmethane or fluorene is due to even greater stability of the resulting radical, as each of them has two  $\pi$ -conjugation systems. In addition, the buildup of tetralin oxidation products, such as tetralol and tetralone, which inhibit the oxidation reaction, also causes an inhibitory effect [42, 66, 72].

According to the assumption advanced in [42, 72], along with the involvement of inhibitor peroxide radicals in chain termination, the resulting polar products of tetralin oxidation can have a solvating effect on high-molecular-mass condensation and dimerization products, thereby preventing their sedimentation; similarly, the introduction of benzyl alcohol into the

fuel reduces the amount of solid deposits, although benzyl alcohol is not an oxidation inhibitor:



Dihydrobenzene can also act as a fuel oxidation inhibitor at its sufficient concentration (above 5000 ppm) in the fuel [73]:



The favorable effect of tetralin and alkylaromatic hydrocarbons on the thermo-oxidative stability of jet fuels is manifested only when their content is low (at most 10%). When the concentration of naphthenoaromatic hydrocarbons reaches 20–50% [24–55, 71, 74], their inhibitory effect is offset by a significant amount of polar products of oxidation of the naphthenoaromatic compounds themselves, with the amount being sufficient for the formation of gum and solid precipitates. An increase in the amount of 2-methylnaphthalene from 0 to 20% in isoparaffin fuel leads to a sharp increase in the induction period of oxidation, but a further increase in the concentration of 2-methylnaphthalene does not result in a change in the induction period [71]. The data obtained at 325°C show unsatisfactory thermal stability of the isoparaffin fuel doped with 25% 2-methylnaphthalene.

According to the mechanism of formation of soluble macromolecular oxidatively reactive species (SMORS) proposed in [33, 75–77], oxidation of fuels begins with the oxidation of traces of phenols or other easily oxidizable compounds (Scheme 1). The resulting resonance-stabilized radical reacts with the peroxide radical to form quinone. Quinones enter into electrophilic substitution reactions with heterocyclic compounds, such as carbazoles (reaction (4a)). The oxidation of the resulting compound leads to the formation of quinone (reaction (5)), which participates

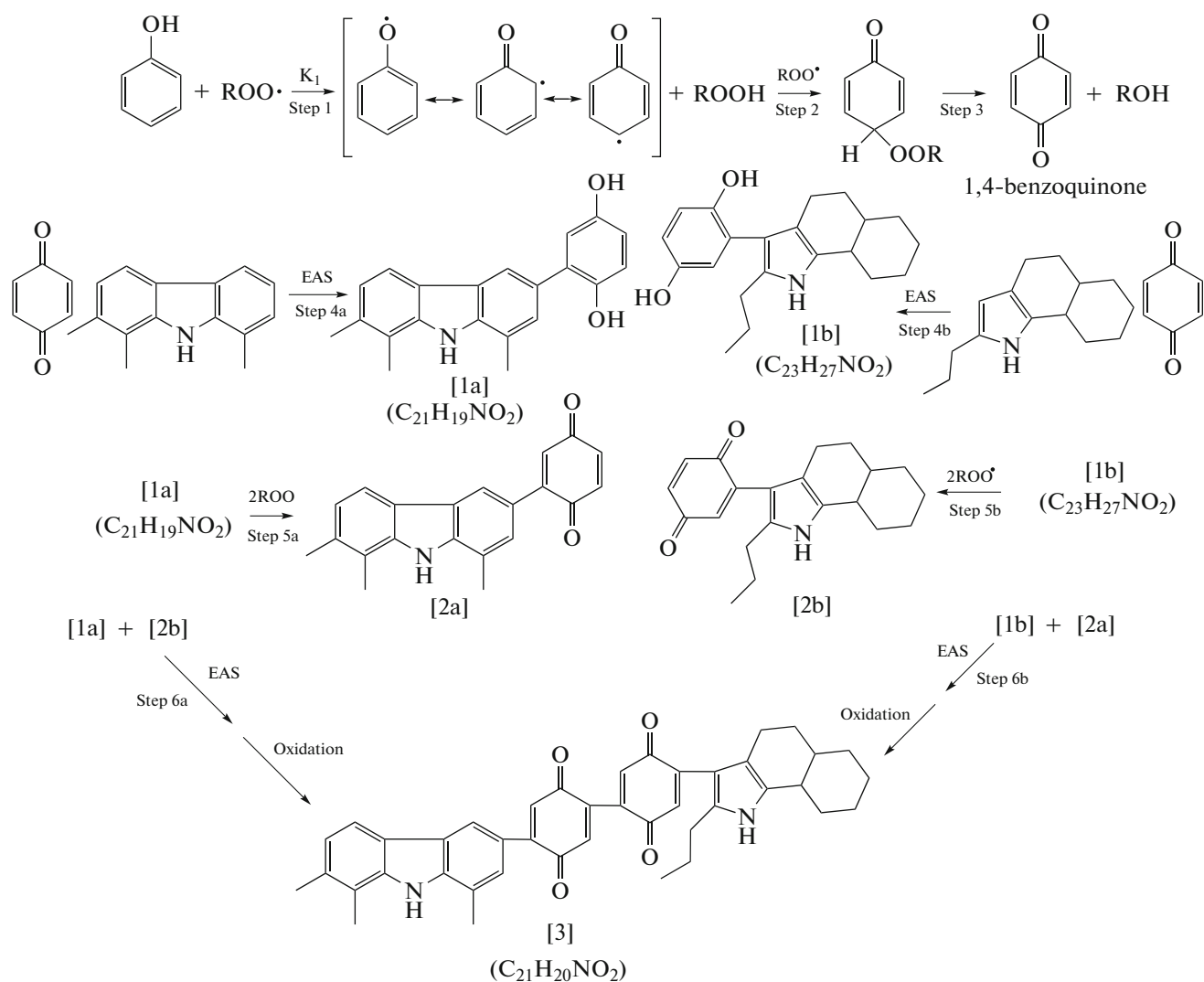
in the electrophilic substitution reaction again, forming high-molecular-mass products. Consequently, nitrogen-containing compounds increase the fuel propensity to oxidation [52]. SMORS have an average molecular weight of up to 400, their participation in condensation reactions leads to the formation of insoluble compounds with an average molecular weight of 600–900 and, next, insoluble deposits [78].

This mechanism is confirmed by the presence of bands due to the carbonyl group in the IR spectrum of the oxidized fuel, as well as by an increase in aromaticity (<sup>1</sup>H NMR) in the order: initial fuel < oxidized fuel < SMORS < precipitate, which indicates the formation of condensed aromatic compounds (3 in Scheme 1). Adding 2,4-dimethylpyrrole to fuel reduces its resistance to oxidation. The introduction of 1,4-benzoquinone and 2-methylindole, precursors of high-molecular products, into the fuel leads to significant precipitation during oxidation at a temperature of 90°C as a result of the formation of quinone–indole oligomers and their further participation in the oxidation process. In favor of the proposed mechanism, there is a correlation between the concentration of phenols, indoles, and carbazoles in the fuel and the amount of deposit [75].

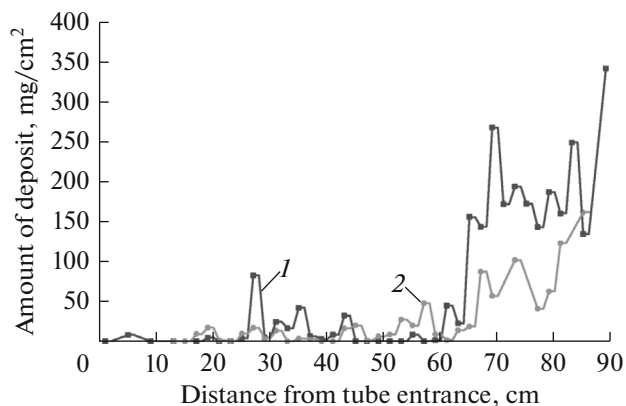
This scheme is confirmed by GC–MS data for the oxidized JP-900 fuel. It contains mainly decalones and decalols with the –OH and the =O group in the α- or β-position [53]. In the deposit, mono- and dicarboxylic acids, hydroxyaromatic compounds, pyrrole derivatives with two–five rings in the molecule, and condensed hydroxyaromatic compounds are present according to HPLC data [63]. The oxidized fuel JP-8 preferably contains aliphatic alcohols (up to 80% of all oxygen-containing oxidation products) and ketones (up to 50%), wherein the –OH and =O groups are at the second, third, or fourth carbon atoms, and dicarboxylic acids [53, 81].

A study of the thermo-oxidative stability of hydrogenated LCO and coal tar fraction separately and in their 1 : 1 mixture by volume showed that the stability of the mixture is four times lower than that of the hydrogenated LCO and about three times lower than the stability of the hydrogenated tar. In other words, negative synergism is observed in compounding of these hydrogenated products: each of the components contains compounds of a certain class that cannot form deposits by themselves, but can interact with compounds of another class [25].

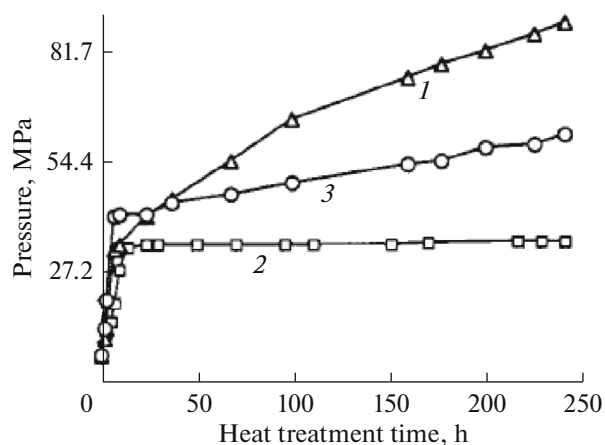
Adsorption purification of fuel with aluminum oxide removes peroxides and nitrogen-containing compounds, thereby certainly enhancing the thermo-oxidative stability [25]. Similarly, the removal of dissolved oxygen from the fuel reduces the concentration of phenol oxidation products (reaction (1) shown in Fig. 12 does not occur; the fuel contains only quinones formed during storage), thereby also increasing stability [78].



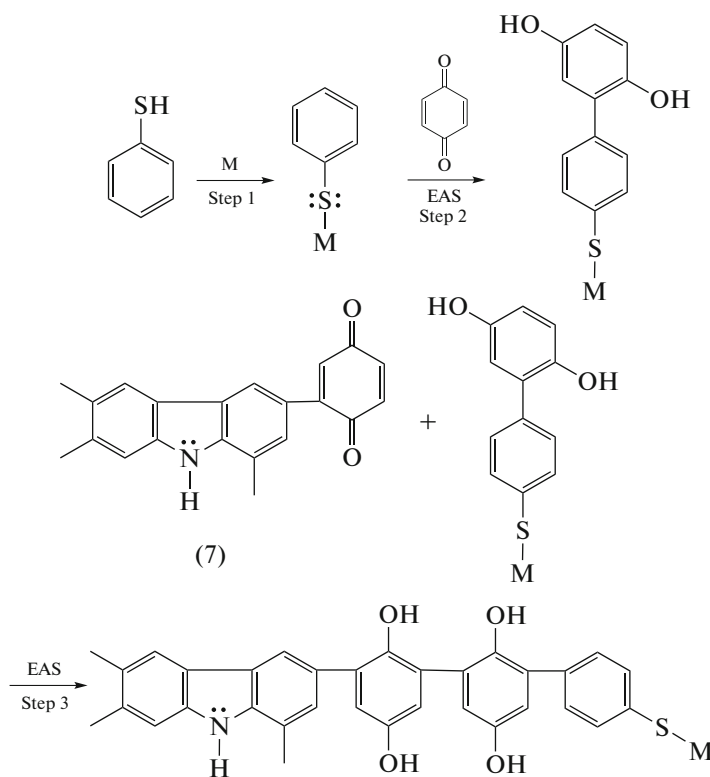
**Scheme 1.** Formation of high-molecular-mass fuel oxidation products in the presence of nitrogen-containing compounds [75].



**Fig. 11.** Thermo-oxidative and thermal stability of JP-8 fuel (1) in pure form and (2) doped with 1 vol % tetralol [42].



**Fig. 12.** Dependence of autoclave pressure on the time of pyrolysis of (1) *n*-decane, (2) tetralin, and (3) ethylcyclohexane [84].



**Scheme 2.** Formation of high-molecular-mass products of fuel oxidation on a steel surface in the presence of nitrogen-containing compounds [33].

When fuel contacts a steel surface [33], the presence of arylthiols, which interact with the surface to form a metal sulfide (Scheme 2), is of decisive importance. The product of the sulfide reaction with quinone further reacts with quinone–indole oligomers to form high-molecular-weight deposits on the surface. Despite the fact that according to some data [79], oxidizable sulfur compounds (mercaptans, disulfides, and sulfides) are able to inhibit the oxidation of fuels, it is reported [80] that aryl sulfides (benzyl phenyl sulfide, methyl phenyl sulfide, and *n*-propyl phenyl sulfide) in a concentration of 1000 ppm on a sulfur basis in the fuel increase the rate of deposit formation both in the presence and absence of dissolved oxygen. The mechanisms illustrated in Schemes 1 and 2 are general, and carbazoles, pyrroles, thiophenols, thiophenes, amines, and thiols can enter the reaction by analogy to indole.

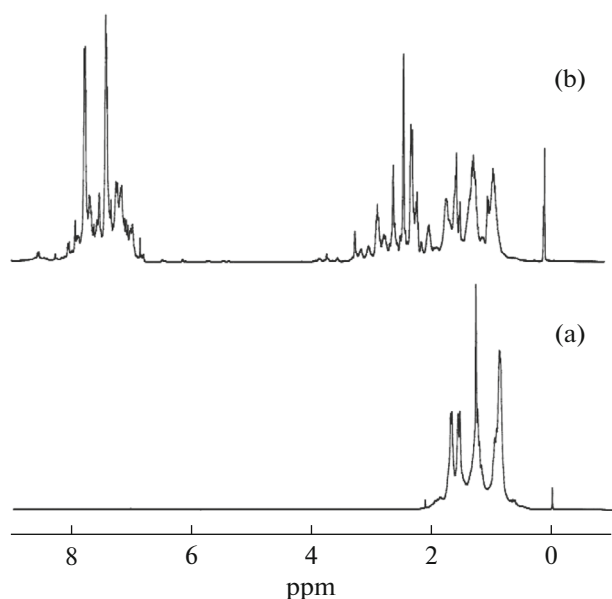
Extensive studies [16, 22, 33] showed that JP-900 fuel has excellent thermo-oxidative stability in comparison with JP-8 samples. The high thermo-oxidative stability of JP-900 was associated in [16, 22] mainly with the absence of heteroatomic compounds in its composition, which are SMORS [75]. However, a comparison of the amount of deposits formed by coal tar fractions and LCO in a heated steel tube in the auto-oxidation regime [54] showed that the hydrogenated fractions are much more stable than the hydrofined fractions, despite the same content of hetero compounds.

The amounts of tube deposit for fuels JP-900, JP-8, and JP-8 + 100 (fuel JP-8 with an antioxidant and detergent–dispersant package) are compared in Fig. 10. In testing JP-900 fuel, the amount of tube deposit is an order of magnitude smaller than in the case of JP-8. In thermo-oxidative stability, JP-900 fuel is superior to the additive-doped JP-8 fuel and similar to JP-7 fuel used in aircraft designed for long super-sonic flight [5].

Similar results were obtained by testing fuels in an advanced aircraft fuel system simulator (AAFSS) [22]. Unlike JP-8, JP-900 fuel almost does not form deposits. Preliminary purging of JP-8 with nitrogen to remove dissolved oxygen leads to a reduction in the amount of deposit to the value observed for JP-900, which is quite expected [54].

The introduction of tetralone or tetralol, native oxidation inhibitors contained in JP-900, into JP-8 fuel increases both thermo-oxidative and thermal stability characterized by the amount of tube deposit (Fig. 11).

The formation of polar high-molecular-mass oxidation products leads to an increase in fuel viscosity as a result of the formation of an entanglement network. For example, the viscosity of oxidized JP-900 fuel at a temperature of  $-65^{\circ}\text{C}$  is two times that of the initial sample. The formation of alcohols and phenols, rather than acids and ketones leads to a more noticeable increase in viscosity [53]. At the same time, oxidation does not affect the pour point. The smoke point of fuel



**Fig. 13.**  $^1\text{H}$  NMR spectra of a hydrogenated mixture of kerosene fractions of LCO and coal tar (a) before and (b) after heat treatment for 4 h at  $480^\circ\text{C}$  [23].

was reported [77] to decrease in the presence of SMORS, and the capacity for forming emulsions (emulsibility) was found [81] to increase in the presence of polar oxidation products acting as surfactants.

#### *Thermal Stability of Jet Fuels*

High fuel temperatures (above  $300^\circ\text{C}$ ) can happen in a fuel–oil heat exchanger. In the engine operating at cruise power, the rate of fuel flow through the heat exchanger is large and the fuel temperature does not reach such values. However, at idle power with a low consumption of fuel, its temperature rises [75] and thermal, not oxidative, transformations of the fuel begin to prevail.

Differences in thermal stability between fuels are due to their hydrocarbon composition. Aromatic hydrocarbons without alkyl substituents are the most thermally stable, as well as naphthenes. Naphthenoaromatic hydrocarbons act as hydrogen donors. Arylaromatic hydrocarbons and alkanes are the least stable [54, 56, 82–84]. Figure 12 shows the relation of pressure in the autoclave to the time of pyrolysis of ethylcyclohexane, *n*-decane, and tetralin at  $450^\circ\text{C}$  [84]. During the pyrolysis of tetralin, there is a pressure increase due to heating of the autoclave at the beginning of the experiment; then, the pressure remains unchanged, indicating the nonoccurrence of gas formation and thermal degradation. *n*-Decane is characterized by the highest reactivity, like other alkanes, and it is this property that determines the unsatisfactory thermal stability of Fischer–Tropsch fuels, the impossibility of using them in pure form as thermostable jet

fuels on one hand, and their use as endothermic fuels on the other hand [85].

As the thermal treatment time of fuel increases, the amount of cyclohexanes, decalins, and alkanes decreases; the concentration of aromatic hydrocarbons, including biphenyls due to the recombination of phenyl radicals, increases; and the concentration of naphthalenes increases as a result of the dehydrogenation of decalins and tetralins [23, 29, 57, 86] (Table 7). The increase in the concentration of aromatic hydrocarbons is also indicated by the  $^1\text{H}$  NMR spectra of the initial and thermally treated fuel (Fig. 13) [23, 86].

The peroxides and hydroperoxides formed during the oxidation of fuel affect the thermal stability of the fuel at a temperature of  $300$ – $500^\circ\text{C}$ . The removal of peroxides by adsorption on alumina increases the thermal stability, expressed by the amount of deposits, of naphthenoaromatic fuel by a factor of 9 at a temperature of  $470^\circ\text{C}$  [87]. Thus, despite the different mechanisms of deposit formation at temperatures below and above  $300^\circ\text{C}$ , the oxidation of fuel during storage and in the fuel system affects its high-temperature behavior. During the testing of fuels containing dissolved oxygen, the oxidation of alkanes occurs in the oxidizing temperature region and the degradation of alkanes and unstable products of their oxidation takes place in the region of thermal transformations. At the same time, decalin and tetralin oxidation products are more stable in the high-temperature region (at  $450^\circ\text{C}$ ) than the oxidation products of alkanes [88].

Special attention should be given to the differences in thermal stability between the main components of naphthenic fuels, *cis*- and *trans*-decalins [82, 85, 89]. The pyrolysis of a mixture of decalins leads to a decrease in the *cis*-isomer content and a slight increase in the *trans*-decalin content (Fig. 14). Under pyrolysis conditions, *cis*-decalin partially isomerizes into the *trans*-isomer and partially undergoes ring opening and cracking of the alkyl chains, as evidenced by the gas yield during pyrolysis of decalins: 5.4 wt % for 4 h at  $450^\circ\text{C}$  for *cis*-decalin and 0.8 wt % from *trans*-decalin under the same conditions [85].

The differences in thermal stability between the decalin stereoisomers are due to the fact that *trans*-decalin is conformationally rigid and the *cis*-isomer is conformationally flexible. Additional differences in stability arise from the presence of gauche-interactions of *cis*-decalin. Thus, the selective hydrogenation of naphthalene fractions to a product with a predominant *trans*-decalin content makes it possible to produce fuels with high thermal stability [90].

Under supercritical conditions, which can occur at a very high speed of flight and a high pressure in the fuel system (up to 10 MPa), the product composition of thermal degradation of hydrocarbons differs from that characteristic of subcritical conditions [91, 92]. Thus, alkanes form a significant amount of high-molecular-mass products that are not observed under



**Table 7.** Changes in the hydrocarbon composition of JP-8 fuels and the hydrogenated kerosene fraction of LCO during heat treatment for 45 min at 480°C [57]

Hydrocarbon group	Hydrogenated LCO fraction		JP-8	
	before heat treatment	after heat treatment	before heat treatment	after heat treatment
Alkanes	18.8	6.7	54.1	13.0
Naphthenes	78.8	52.0	16.6	11.1
Alkenes	2.0	0.4	3.5	1.0
Naphthenoaromatics	<0.1	7.5	0.3	5.5
Alkylbenzenes	0.4	9.7	19.0	33.6
Biphenyls	<0.1	5.8	0.4	2.4
Naphthalenes	<0.1	6.7	6.2	14.7
Fenanthrenes	<0.1	0.4	<0.1	0.3
Pyrenes and more condensed HCs	<0.1	<0.1	<0.1	0.4

subcritical conditions. The pyrolysis of butylbenzene and butylcyclohexane gives a considerable amount of diphenylalkanes. Decalin and tetralin are mainly converted to isomerization products (spiro [4,5]decane, 1-methylperhydroindan, 1-methylindan), whereas cracking and dehydrogenation products dominate in the case of pyrolysis under subcritical conditions. The rate constants of pyrolysis of tetradecane, butylbenzene, butylcyclohexane, decalin, and tetralin at 450°C are 1.67, 1.72, 0.313, 0.132, and 0.037 h<sup>-1</sup>, respectively [91].

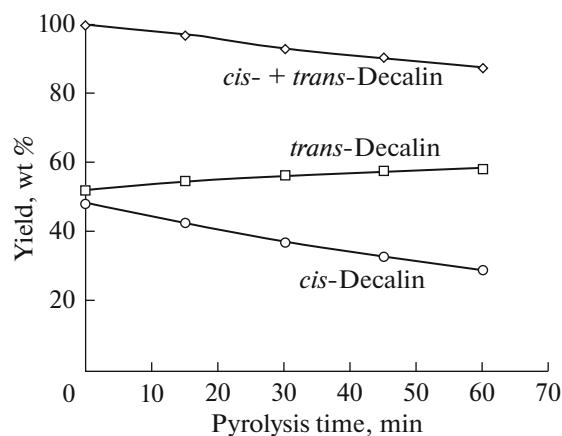
A statistical analysis of 27 jet fuel samples [23] showed that the amount of solid deposits formed at a temperature of 480°C increases linearly with the concentration of alkanes, tends to decrease with increasing tetralin and decalin contents, has an implicit tendency to decrease with increasing cyclohexane content, and does not depend in any way on the concentration of aromatic hydrocarbons. The latter two features are due to the fact that the stability of hydrocarbons of these classes depends significantly on the presence of alkyl substituents in their molecules. Thermal stability decreases as the length of the substituent chain increases, and compounds with several alkyl substituents are more stable than those with one substituent with the same total number of carbon atoms [84].

The presence of alkyldecalins in the hydrogenated kerosene fraction of LCO is responsible for its lower thermal stability compared to the hydrogenated coal tar fraction, which almost does not contain alkyl-substituted naphthenes and aromatic hydrocarbons [23, 29]. Alkyldecalins undergo dealkylation followed by condensation and the formation of tri- and tetracyclic hydrocarbons [86]. In addition, LCO contains a certain amount of alkanes, which also cause a lower thermal stability of the hydrogenated product.

The stability of noncage naphthenes decreases with increasing number of cyclic units. Thus, the thermal

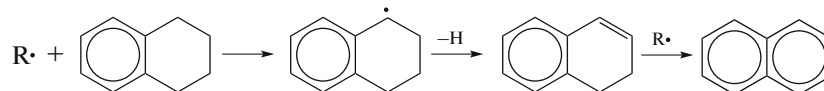
stability of fuel decreases with an increase in the total concentration of noncage tricyclic hydrocarbons [54, 55]. Apparently, this is due to a high molecular mass of the produced radicals, which form hexacyclic compounds—immediate coke precursors—by recombination.

A comparative analysis of the thermal stability of hydrocarbons of different classes clearly shows that JP-900 is superior to JP-8 fuel in stability in the high-temperature region. When the JP-8 and JP-900 fuels are heated in an autoclave at 450°C for 4 h, the yields of the solid residue are 3.3 and 0.2%, respectively, and gas yields are 28.3 and 13.9%; the Fischer–Tropsch paraffin fuel is characterized by the maximum yield of solid residue and gas (3.5 and 34%, respectively) [58, 74, 82]. It is reported [83] that JP-900 fuel is more thermostable than the specialty thermostable fuels JP-TS and JP-7. Figure 15 shows the dependence of the yield of gas and liquid phase on the duration of

**Fig. 14.** Redistribution of decalin stereoisomers during pyrolysis (450°C) [82, 89].

heat treatment of petroleum-derived JP-8 fuel and JP-8C fuel derived from coal distillate [84].

The excellent thermal stability of fuels obtained by hydrotreating high-aromatic feedstock is partly due to the presence in them of naphthenoaromatic hydrocarbons, which are hydrogen donors [82, 83, 85, 93, 94].



Scheme 3.

Not all naphthenoaromatic compounds show hydrogen donor properties. For example, 1,2,3,4,5,6,7,8-octahydrophenanthrene and 5,6,7,8-tetrahydroisoquinoline [93] are ineffective from the viewpoint of inhibiting thermal transformations of hydrocarbons. The possibility of involving a compound in hydrogen transfer is determined not only by the presence of weak C–H (N–H) bonds in the molecule, but also by the formation of a resonance-stabilized radical. If the radical formed is not stabilized by resonance, it participates in a number of transformations, and the compound is rapidly consumed, which is typical, in particular, for tetrahydroisoquinoline.

In addition to tetralin, 1,2,3,4-tetrahydroquinoline, dihydrophenanthrene, 1,2,3,4-tetrahydro-1-naphthol, etc. exhibit similar hydrogen-donor properties (Fig. 16). Tetrahydroquinoline is a more efficient hydrogen donor than tetralin: hydrogen transfer from tetrahydroquinoline begins with the degradation of the C–N bond, which is less strong than the C–H

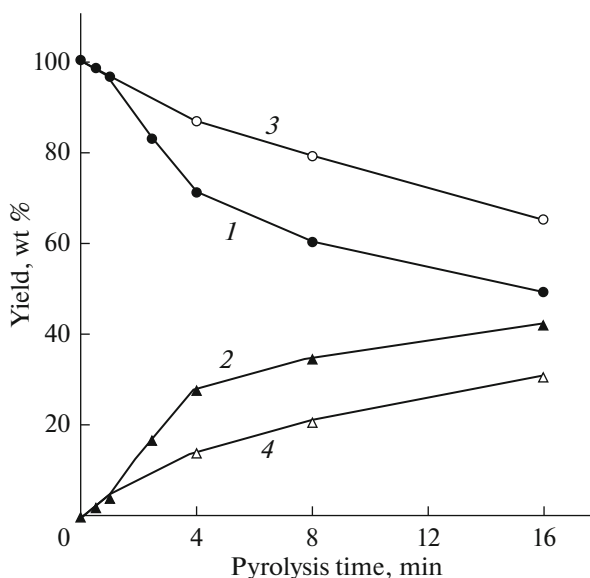
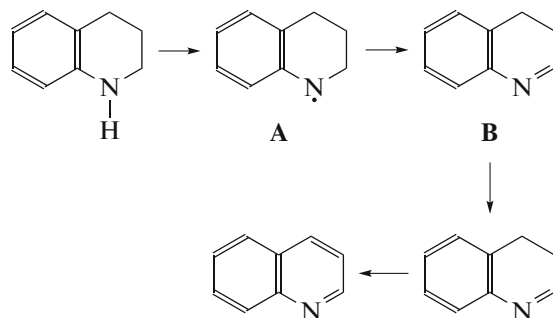


Fig. 15. Yields of the (1, 3) liquid phase and (2, 4) gas during the heat treatment of (1, 2) JP-8 and (3, 4) JP-8C fuels [84].

The lower dissociation energy of C–H bonds at the carbon atom in the  $\alpha$ -position to the aromatic ring, in comparison with other C–H bonds, along with the possibility of stabilization of the radical formed during pyrolysis, predetermines the possibility of inhibiting the thermal degradation of hydrocarbons [82, 83, 85, 95]:

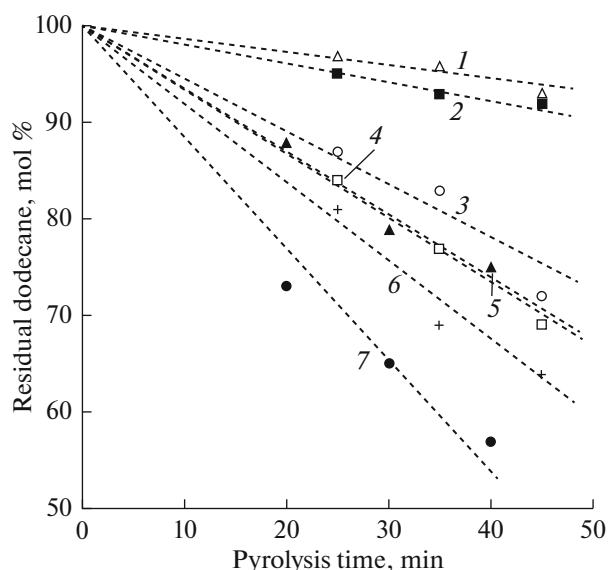
bond [93] (Scheme 4). At the same time, as shown in [95], the introduction of tetrahydroquinoline in a concentration of 1–2.5% into JP-8 fuel leads to deterioration of thermo-oxidative stability in the temperature range of 180–300°C. Thus, the amount of tube deposit increases by a factor of almost 9, but the amount of deposit in the high-temperature region (500–550°C) is reduced by a factor of ~1.5. Similarly, the addition of the hydrogen donors tetralin and a mixture of tetralin and tetralone to dodecane reduces the amount of deposit only in the high-temperature region, the amount of tube deposit at temperatures up to 450°C remains almost unchanged (Fig. 17). The total amount of tube deposit and the gas yield decrease. For example, the yields of gas and solid deposit in pure dodecane are 5.32% and 174 ppm, respectively, and those for its 1 : 1 mixture with 1% tetralin/tetralone are respectively 2.31% and 123 ppm [96].



Scheme 4.

In addition, the introduction of a mixture of tetralin and tetralone, the most efficient hydrogen donor according to the test results [96], significantly changes the product composition of fuel degradation at a high temperature (772°C) [97]. The concentration of aromatic entities in the product formed in the presence of the additive is less by 32%, and the number of carbon atoms that “bridge” aromatic rings decreases by 62%.

The participation of tetralin in hydrogen transfer during the pyrolysis of jet fuels is confirmed by the following finding [82, 83]. Pure tetralin is extremely stable under pyrolysis conditions, as only 4% naphtha-



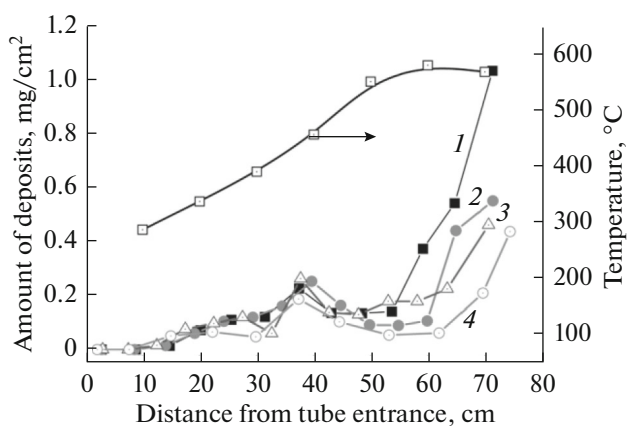
**Fig. 16.** Effect of hydrogen donors added in an amount of 10 wt % on the conversion of dodecane at 450°C: (1) tetrahydroquinoline, (2) dihydrophenanthrene, (3) tetrahydro-1-naphthol, (4) tetralin, (5) benzyl alcohol, and (6) phthalane; (7) additive-free dodecane [93].

lene and 12.7% 1-methylindan are produced for 4 h at 450°C (Fig. 18). When a hydrocarbon that is not characterized by thermal stability, for example tetradecane or butylbenzene, is added to tetralin, the product composition of tetralin conversion changes fundamentally: the dehydrogenation reaction yielding naphthalene proceeds to a great extent. As the tetralin concentration in the mixture is increased from 10 to 25%, the proportion of the isomerization product slightly increases. In other words, when tetralin is in an insufficient amount, alkyl radicals abstract hydrogen atoms from the  $\alpha$ -carbon atom; this reaction is principal, and the excess of tetralin relative to the alkyl radicals creates conditions for the tetralin isomerization reaction.

Figure 19 shows the amount of solid deposit produced by the heat treatment of tetralin-doped JP-8 fuel [82]. The hydrogen donor additive exhibits the greatest efficiency in a concentration of up to 10%. It should be emphasized here that at a higher tetralin content, the fuel begins to be intensely oxidized because of the low oxidative stability of tetralin [67].

The analysis of solid deposits formed by the thermal degradation of JP-8 fuel and hydrogenated kerosene fraction of LCO using solid-state  $^{13}\text{C}$  NMR spectroscopy (Table 8) showed that the deposits have identical very high aromaticity and aliphatic carbon atoms are represented only by bridges linking the aromatic rings [86]. The concentration of heteroatoms does not exceed 0.5%.

The introduction of hydrogen donor additives leads to a change in morphology of carbon deposits [96–



**Fig. 17.** Effect of hydrogen donors on the distribution of deposits in the tube during heat treatment of dodecane: (1) additive-free dodecane, (2) 1% benzyl alcohol, (3) 1% tetralin, and (4) 0.5% tetralin + 0.5% tetralone [96].

98]. Pyrolysis of JP-8 fuel with the addition of a 2% mixture of tetralin and tetralone leads to the formation of filament carbon, whereas pyrolysis of the additive-free fuel produces amorphous carbon and short carbon filaments of a large diameter (Fig. 20) [97]. Filamentous carbon is a product of catalytic reactions of metals (Ni and Fe) with fuel degradation products. Amorphous carbon or large-diameter filaments are formed by the buildup of PCA on the surface, which leads to termination of filament growth reactions. Inhibition of PCA formation by the introducing a hydrogen donor additive creates conditions for the growth of carbon filaments. Thus, deactivation of the metal surface and introduction of hydrogen donors can ensure noticeable inhibition of deposit formation. The morphology of the deposits also depends on the composition of the initial fuel, for example, on the ratio of the hydrogenated LCO fraction and coal tar [99].

Concluding the analysis of hydrogen donor properties of some components of jet fuels, we should note that naphthenoaromatic distillates obtained by partial hydrogenation of coal tar or pyrolysis tar hold promise for use as additives enhancing both the thermal and thermo-oxidative stability of petroleum-based jet fuels [42, 72, 93, 94, 100]. However, the possibility of stabilizing fuels is limited to a temperature of 400–450°C for their application. Thus, the half-time of conversion of dodecane in a feed mixture containing 10% tetrahydroquinoline is 5 h at 450°C, 12 min at 500°C, and 45 s at 550°C [94].

It should also be pointed out that the available data on the effect of naphthenoaromatic and aromatic hydrocarbons on the thermo-oxidative and thermal stability of jet fuels are controversial. Some researchers [93, 94] report a decrease in the conversion of alkanes in the presence of tetralin or tetrahydroquinoline; others [95], on the contrary, note an increase in the con-

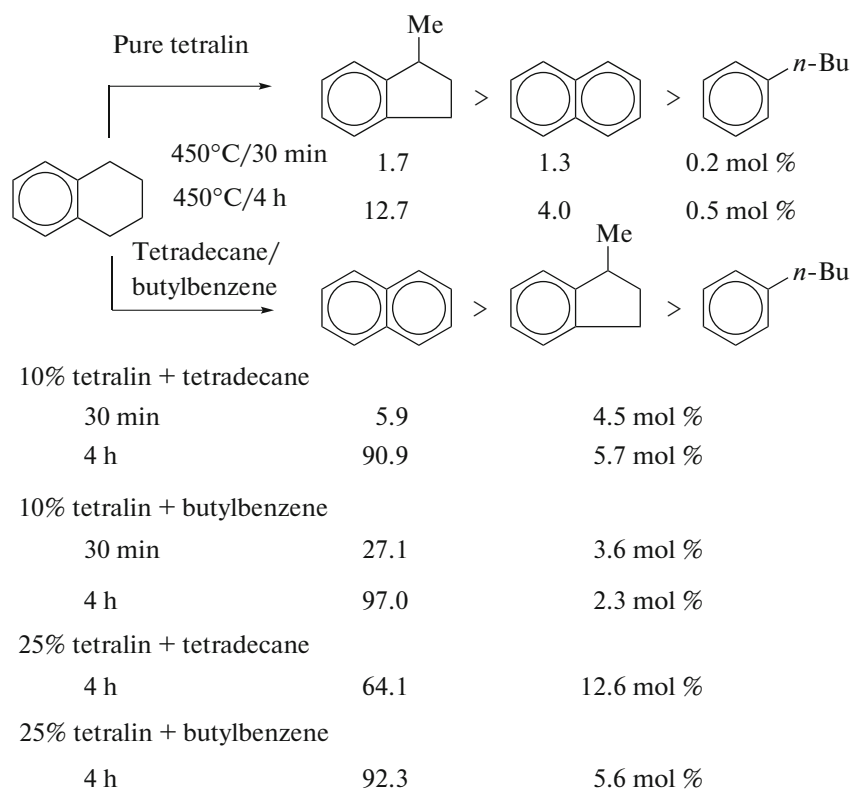


Fig. 18. Distribution of the products of pyrolysis of tetralin in pure form and in mixture with hydrocarbons [82, 83].

version of alkanes and simultaneous decrease in both the amount of deposit and the aromatics content in the thermolysis products. The participation of a compound in the inhibition of thermal degradation can be accompanied by enhancement of fuel oxidation in the presence of this compound, as shown by the example of tetrahydroquinoline [95]. The inhibition of fuel oxidation at 140°C by introducing methylnaphthalenes

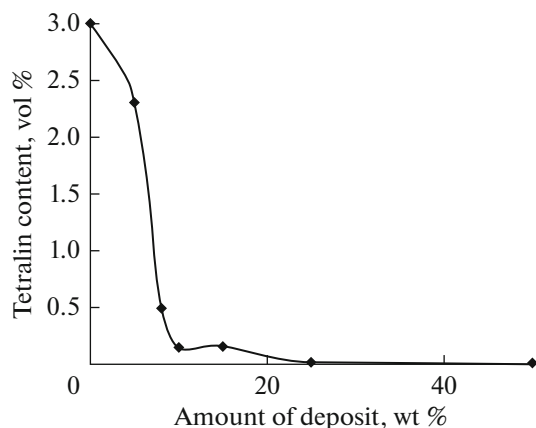


Fig. 19. Amount of solid deposits in the pyrolysis of tetralin-doped JP-8 fuel (450°C, 4 h) [82].

leads to a serious increase in the amount of tube deposit in a pyrolytic regime (325°C) [71].

The analysis of the composition–property relations for jet fuels derived from highly aromatic feedstock shows that the most desirable components are naphthoaromatic hydrocarbons (up to 10%), bicyclic naphthenes (from the viewpoint of thermal and thermo-oxidative stability, density, volumetric calorific value, low-temperature properties), and isoalkanes (from the viewpoint of combustion efficiency and minimization of soot formation) [101]. Based on the analysis of a large sample of jet fuels, Butnark [23] proposed a triangular diagram to optimize the fuel composition.

Obviously, JP-900 fuel is not the only representative of naphthenic fuels. Although the comparison of different fuels is not entirely correct because of their different fractional and hydrocarbon compositions, it can be noted that the specific calorific value of JP-900 fuel is not very high, which is due to a low paraffin content in it. By varying the feedstock composition and the hydrogenation depth, it is possible to obtain a number of fuels differing in fractional composition, density, thermo-oxidative stability, and calorific value that meet the requirements of a particular task.

Along with the fuels having a wide fractional composition discussed in this section, narrow hydroge-

**Table 8.** Solid-state  $^{13}\text{C}$  NMR data for the solid products of pyrolysis of JP-8 fuel and hydrogenated kerosene fraction of LCO [86]

Property	Hydrogenated LCO fraction	JP-8
Proportion of aromatic carbon atoms	0.97	0.98
Proportion of unprotonated aromatic carbon atoms	0.55	0.51
Proportion of quaternary carbon atoms	0.51	0.49
Average number of rings in conjugated aromatic moieties	7	6
H/C ratio	0.54	0.56

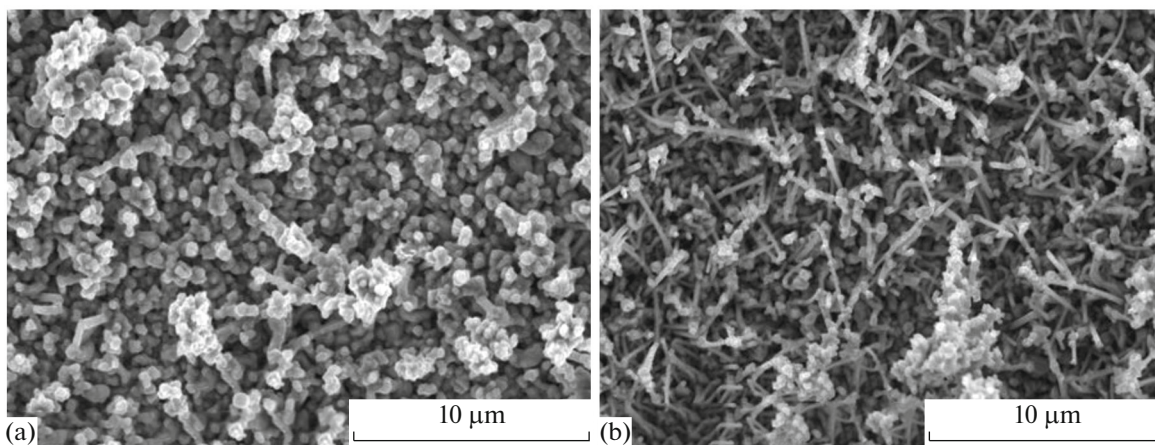
nated fractions of various highly aromatic wastes may be of interest. In particular, decahydroacenaphthene has a density of  $955 \text{ kg/m}^3$ , the pour point below  $-60^\circ\text{C}$ , and the volumetric calorific value of  $40\,414 \text{ kJ/L}$  [102]. It should also be mentioned that high-energy fuels, represented by oligomers and co-oligomers of cyclopentadiene, and its alkyl derivatives, indene [1, 6, 103–107], can be obtained from highly aromatic olefin-containing pyrolysis and coking wastes.

#### *Composition and Performance Characteristics of Diesel Fuels Obtained by Hydrogenation of High-Aromatic Waste*

Requirements for diesel fuels are substantially different from those for aviation kerosene. The main difference is in the oxidation stability—this characteristic is inversely proportional to the cetane number (CN) of the diesel fraction. Therefore, the high thermo-oxidative stability of naphthenic fuels is expressed in unsatisfactory ignition by compressing the fuel–air mixture. For this reason, the creation of a single fuel for military equipment (for gas turbine and diesel engines) based on JP-900 is impossible without the use of cetane-boosting components and additives [108].

Data on the cetane number, viscosity, and density of some model diesel hydrocarbons [109–111] are given in Table 9. As can be seen, naphthenes (cyclohexanes and decalins with or without short alkyl substituents) and naphthenoaromatic hydrocarbons are characterized by low CN values, determining a generally low cetane number of the resulting diesel fuel. This, in turn, is expressed in the complication of diesel engine startup and warm-up at low ambient temperatures [112]. The diesel cetane number of naphthenic–aromatic fuels decreases from 41 to 27 with increasing concentration of aromatic hydrocarbons from 4 to 42% and increases with increasing the amount of paraffinic–naphthenic HCs and hydrogen content in the fuel [113]. For aromatic hydrocarbons, the hydrogen content in the molecule and the cetane number increase with the proportion of aliphatic carbon atoms in alkyl substituents (see Figs. 21, 22) [110, 113]. An increase in the proportion of *cis*-decalin in a mixture of stereoisomers promotes an increase in the cetane number [111], which is due to the lower oxidation stability of the *cis*-isomer.

From Figs. 26 and 27 it can be seen that the exhaustive hydrogenation of highly aromatic feedstock does not eliminate the problem of the unsatisfactory cetane value of the obtained diesel fuel, since unsubstituted



**Fig. 20.** Scanning electron microscopy images of carbon deposits on the surface of Inconel 718 steel after heat treatment of JP-8 fuel for 24 h at a maximum temperature of  $500^\circ\text{C}$ : (a) the additive-free fuel and (b) the fuel doped with 2% mixture of tetralin and tetralone [97].

**Table 9.** Cetane number, viscosity, and density of some model diesel hydrocarbons [109–111]

Hydrocarbon	Density at 20°C, kg/m <sup>3</sup>	Kinematic viscosity at 30°C, mm <sup>2</sup> /s	Cetane number
<i>n</i> -Tetradecane	762.0	2.484	97
Ethylcyclohexane	786.4	0.947	34
<i>n</i> -Hexylbenzene	856.2	1.636	32
<i>n</i> -Hexylcyclohexane	807.3	2.230	65
<i>n</i> -Dodecylcyclohexane	822.3	7.077	85
1-Methylnaphthalene	1020	2.603	0
Tetralin	967.1	1.899	21
Phenylcyclohexane	941.1	2.399	4
<i>trans</i> -Decalin	870.2	2.044	32
<i>cis</i> -Decalin			42
Bicyclohexyl	887.2	3.596	50

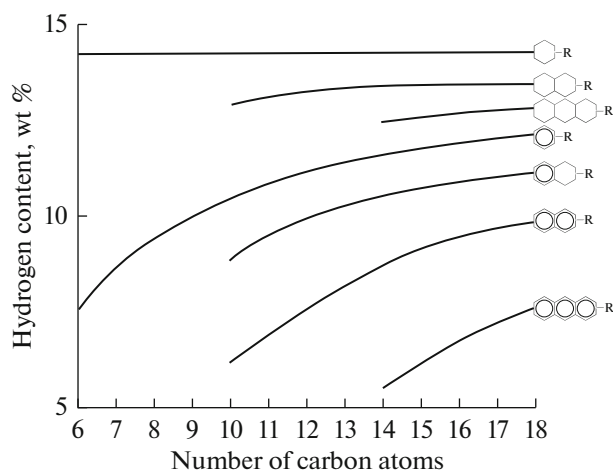
decalins do not have a high cetane number. One solution to this problem can be either the alkylation of aromatic hydrocarbons followed by hydrogenation of the alkylate [114] or the hydrocyclization of decalins, tetralin, perhydroindan, or tricyclic naphthenes [115–119].

In the processing of high-aromatic feedstock, the yield of the 180–360 or 200–320°C diesel distillate is within the range of 46–76% of feedstock (without isolation of the kerosene fraction or, otherwise, less) depending on its fractional composition and the severity of the technological regime [120–123]. The diesel fraction has a density in the range of 820–900 kg/m<sup>3</sup>, contains less than 350 ppm of sulfur, and exhibits excellent low-temperature properties, but a low cetane value within 38–48. Table 10 lists the main characteristics of diesel fuels, obtained from coal liquefaction

distillate and coal semicoking tar, according to published data [124–128].

The main differences from petroleum-based diesel fuel, which consist in better low-temperature properties, higher density, and a smaller cetane number, are due to the unique fuel composition represented mainly by naphthenic hydrocarbons, the content of which varies within the range of 67–88%, depending on the hydrogenation depth; the amount of alkanes does not exceed 9%. The main hydrocarbons of diesel produced from high-aromatic distillates are alkyltetralins (6-methyltetralin, 2,6-dimethyltetralin), tetrahydroanthracene, perhydroanthracene, decalins, and their alkyl derivatives (2-methyldecalin, 2,6-dimethyldecalin, 2-ethyldecalin), bicyclohexyl, hexahydroindan, alkylcyclohexanes, and a small amount of alkanes (tridecane, tetradecane, etc.) [121, 123, 125, 129, 130]. At the same time, the main hydrocarbons of petroleum-based diesel are alkanes and alkylaromatic hydrocarbons. It should be noted, however, that the diesel fuel manufactured from shale distillate contains alkanes in a high concentration (60%) [126], which is in general typical of fractions obtained by the pyrolysis of oil shales.

The importance of solving the problem of increasing the CN of naphthenoaromatic diesel fuels is dictated by the influence of this characteristic on a number of diesel operation parameters, including not only engine startup, but also emissions of toxic gases [131–135]. A low cetane number leads to a longer ignition delay, which in turn is expressed by the presence of sufficient time for mixing fuel and air and burning the fuel in a well-prepared mixture with a large heat release at the start of combustion. Accordingly, a high temperature in the combustion chamber causes an increase in nitrogen oxide emissions in comparison with petroleum diesel fuel [56, 131, 132, 135] because the thermal mechanism of the formation of nitrogen oxides comes into play [46]. At the same time, good mixing of the fuel–air mixture before ignition excludes



**Fig. 21.** Relation of the hydrogen content in the molecules of naphthenic and aromatic hydrocarbons to the number of carbon atoms [110].

the formation of foci of a rich mixture and, consequently, reduces the emissions of soot particles [132]. As an example, Fig. 23 presents data on  $\text{NO}_x$  and particulate emissions of petroleum diesel fuel, the diesel fraction obtained by hydrotreating the coal liquefaction product, and its blends with biodiesel. An increase in the aromatics content of fuel leads to an increase in particulate matter emissions, which has already been discussed in relation to jet fuels.

The prevalence of bi- and tricyclic hydrocarbons in the diesel composition is manifested in an increase in emissions of unburned hydrocarbons [131]. However, Zhuang et al. [132] did not reveal explicit dependence of CO and HC emissions on the composition of the blend of naphthoaromatic fuel with biodiesel, the emissions of these substances are determined to a greater extent by the diesel load and the timing of the fuel injection advance. Ogawa et al. [136] reported a reduction in emission of particulate matter by introducing decalin into petroleum-based diesel fuel.

The aforementioned research groups [133, 134, 136] report a decrease in  $\text{NO}_x$  and particulate matter emissions in the case of using a diesel derived from highly aromatic feedstock, as compared to the petroleum diesel fuel (Fig. 24). It was also found that an increase in the concentration of naphthenic–aromatic distillate in a mixture with petroleum diesel favors reduction of  $\text{NO}_x$  emissions. The controversial data on nitrogen oxide emissions seem to be due to different compositions of the samples of petroleum diesel fuel used for comparison.

The reduction of nitrogen oxide emissions in the case of using naphthoaromatic fuels can be facilitated by implementing multistage fuel injection [127], and the recycle of exhaust gases can decrease the emissions of nitrogen oxides, carbon monoxide, and unburned hydrocarbons [134]. The cetane number of coal-based diesel fuel and its blends with petroleum diesel can be increased by using ignition promoters, such as ethylhexyl nitrate [137], acetone, *tert*-butyl peroxybenzoate, and isooctyl nitrate [138].

The diesel fuel derived from highly aromatic feedstock is characterized by a higher specific fuel con-

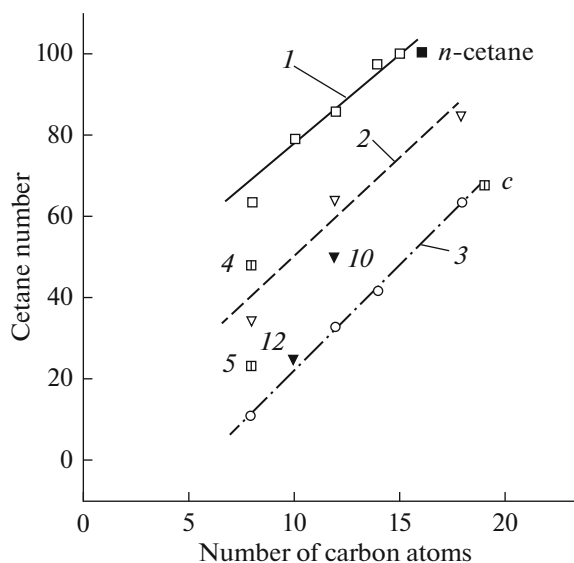


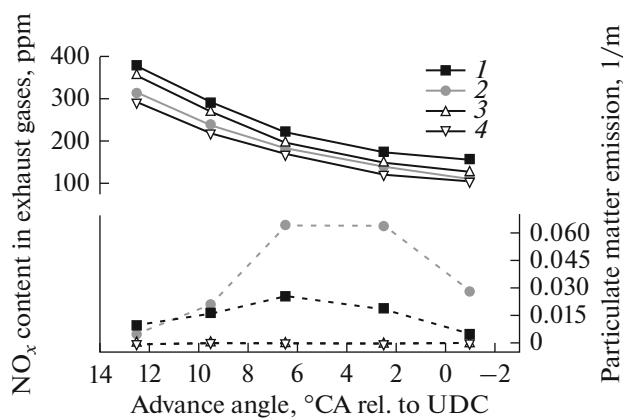
Fig. 22. Dependence of the cetane number of hydrocarbons on the number of carbon atoms in the molecule: (1) alkanes; (2) naphthenes, and (3) aromatics [113].

sumption and lower thermal efficiency [137] as compared with petroleum diesel fuel, the differences that are associated with incomplete combustion of naphthoaromatic and, especially, aromatic hydrocarbons. However, according to other data [132], the differences are insignificant and not obvious.

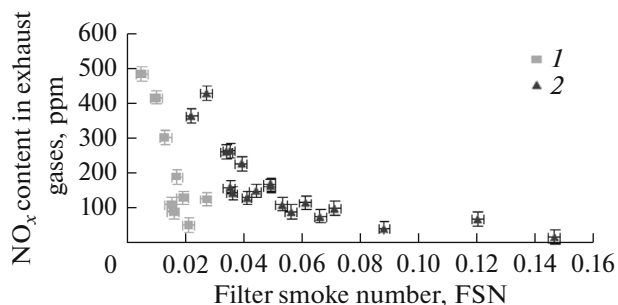
Figure 25 shows the heat release characteristics of diesel obtained from a highly aromatic coal distillate and its mixtures with petroleum diesel fuel [133]. As can be seen, the ignition delay in the case of coal-based diesel is significant, and the burning time defined as the difference between CA10 and CA90 (CA10 and CA90 are the crankshaft angles of  $10^\circ$  and  $90^\circ$ , respectively) is reduced due to the ignition delay and greater volatility of the coal-derived fuel having a lighter fractional composition. The delay in the combustion onset causes a reduction in the thermal efficiency at low loads, but this problem is easily solved by

Table 10. Main characteristics of diesel fuels derived from coal liquefaction distillate and coal semicoking tar [124–128]

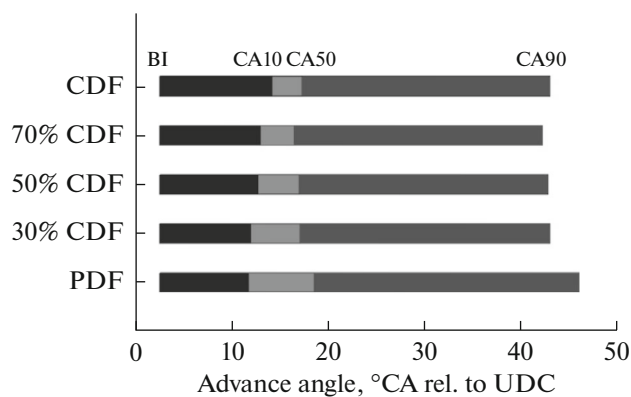
Property	Diesel from coal liquefaction product	Diesel from coal semicoking tar
Density at 20°C, kg/m <sup>3</sup>	814–900	845
Sulfur content, ppm	2–25	6
Cetane number	38–48	46
Kinematic viscosity at 20°C, mm <sup>2</sup> /s	2.02–3.00	4.80
Lower calorific value, kJ/kg	45500	n/d
Carbon residue, wt %	0.17	<0.01
Pour point, °C	–53	–8
Cold filter plugging point, °C	–31	n/d



**Fig. 23.** Emissions of  $\text{NO}_x$  (solid curves) and soot particles (dashed curves) for (1) petroleum-based diesel fuel, the (2) diesel fraction obtained by hydrotreating the coal liquefaction product, and blends of this fraction with (3) 20% and (4) 40% biodiesel [132].



**Fig. 24.** Correlation of  $\text{NO}_x$  emissions with emissions of particulate matter for (1) petroleum diesel fuel and (2) diesel fuel derived from coal distillate [134] (filter smoke number (FSN) characterizes emission smokiness).



**Fig. 25.** Characteristics of the heat release rate of coal-derived diesel fuel and its blends with petroleum diesel fuel: BI is the beginning of injection, CDF is coal-derived diesel, and PDF is petroleum-derived diesel [133].

increasing the fuel injection advance angle in modern fuel delivery systems.

The carbon residue of diesel fuel increases with the PCA content. However, according to Clifford et al. [137], the dependence of the carbon residue of petroleum diesel fuel with fluorene additives on the fluorene concentration passes through a minimum at a fluorene concentration of 1 wt %. In this concentration region, the hydrogen donor properties of fluorene are realized, i.e.  $\text{H}^\bullet$  radicals participate in the stabilization and prevention of recombination of PCA radicals. With a further increase in the concentration of fluorene, the amount of radicals generated from it increases and they combine to form hexacyclic hydrocarbons; as a result, the carbon residue of the fuel increases.

The excellent low-temperature properties of diesel derived from highly aromatic feedstock allow its use as an additive to petroleum-based diesel fuels in order to reduce their pour point and the cold filter plugging point (CFPP) [125]. The pour point depression and CFPP increase with the concentration of coal-derived diesel in the mixture. The characteristics of blends of petroleum diesel fuel with the fuel derived from the coal liquefaction product are summarized in Table 11. The introduction of the coal-derived diesel in a concentration of 40 wt % makes it possible to reduce the kinematic viscosity of the blend, the pour point to  $-31^\circ\text{C}$ , and the CFPP to  $-15^\circ\text{C}$  with an acceptable loss of the cetane number.

A promising means for reducing emissions of nitrogen oxides and incomplete combustion products [132] and increasing CN [139] is compounding of coal-derived diesels with biodiesel—fatty acid esters. The introduction of 1 vol % biodiesel into the diesel fraction obtained from the coal liquefaction product increases the CN by 2 points on average and improves the lubricating properties of the fuel with an insignificant deterioration of the cold-flow properties (Table 12). Adding up to 20% coal-derived diesel fuel to biodiesel [130] or to its mixture with petroleum diesel fuel [140] increases the heat of combustion and thermo-oxidation stability and improves low-temperature properties.

Thus, the main drawback of diesel fuels obtained from highly aromatic feedstocks, i.e., the unsatisfactory value of the cetane number, can be effectively eliminated by introducing additives, blending with biodiesel, or compounding with other diesels. In this aspect, the main advantage of naphthoaromatic diesel, its excellent low-temperature properties, makes it an extremely attractive diesel fuel component and extends the choice of components for compounding. Considered as the components in question can be petroleum-based diesels, Fischer–Tropsch distillates, and products of transesterification and hydroprocessing of oil and fat raw materials.



**Table 11.** Characterization of mixtures of petroleum diesel fuel with fuel derived from coal liquefaction distillate [125]

Concentration of fuel, obtained from coal liquefaction distillate, in the mixture, wt %	Density at 20°C, kg/m <sup>3</sup>	Kinematic viscosity at 40°C, mm <sup>2</sup> /s	Cold filter plugging point, °C	Pour point, °C	Sulfur content, ppm	Cetane number
0	814.0	2.279	−2	−7	310	53
10	817.9	2.271	−8	−17	280	51
20	822.6	2.260	−11	−25	249	50
30	827.6	2.219	−13	−29	216	50
40	832.8	2.192	−15	−31	187	49

**Table 12.** Characterization of diesel fuel derived from the coal liquefaction product with 1 vol % admixture of fatty acid esters [139]

Property	Additive-free	Methyl palmitate	Methyl stearate	Ethyl stearate	Methyl oleate
Density at 20°C, kg/m <sup>3</sup>	860.0	860.1	860.5	860.0	860.3
Kinematic viscosity at 40°C, mm <sup>2</sup> /s	2.02	2.04	2.03	2.05	2.04
CFPP, °C	−31	−30	−30	−30	−30
Pour point, °C	−54	−52	−52	−51	−52
Cetane number	44.0	45.9	46.0	45.8	45.5
Calorific value, kJ/kg	46018	45500	45523	45570	45532
Lubricity—wear scar diameter at 60°C, μm	630	n/d	514	n/d	n/d

## CONCLUSIONS

The significant number of studies on fuels derived from highly aromatic distillates suggests that the tasks of developing thermostable naphthenic jet fuels are still demanding. The following promising areas of research can be noted: selective hydrogenation to obtain fuels with prevalence of certain stereoisomers, regulation of the composition of blended feedstock in order to use the potential of individual sources of raw materials to the maximum extent, improvement of the stability of petroleum fuels using naphthenoaromatic additives, and optimization of fuel composition depending on the desired characteristics.

There are many ways to optimize the fuel composition: controlling the conversion of naphthenoaromatic and aromatic hydrocarbons, compounding feedstocks of different natures, compounding products, and isolating products with a narrow fractional composition. The choice of one or another line of research depends on the criterion of optimization, since the improvement of some properties of fuels (for example, thermo-oxidative stability) often leads to deterioration of others (soot formation).

The use of advanced analytical techniques, such as GC–GC [141–147], HPLC in combination with GC–MS [145], GC/TOF-MS [146], and ESI-MS [147], for analysis of jet fuels extends the possibilities of optimization of their composition. In particular, it

becomes possible to accurately analyze the hydrocarbon-group composition [141, 143] and distribution of sulfur- and oxygen-containing compounds (including phenols) [144, 147], to predict thermo-oxidative stability and lubricating properties from these data, to study the distribution of individual hydrocarbons by narrow fractions [146] and improve the fractional composition of fuel on the basis of these data, and to analyze fuel samples after storage to identify polar compounds [145]. Thus, scientific foundations are being created for optimizing the composition of the fuel and predicting its performance properties [142], which is extremely important in the case of having several initial components for compounding and/or feedstock sources.

## ACKNOWLEDGMENTS

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