

EFFECT OF NAPHTHENOAROMATIC HYDROCARBONS ON THE
OXIDIZABILITY OF HYDROTREATED RT JET FUELV. M. Veselyanskaya, E. D. Radchenko,
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The oxidation susceptibility of jet fuels and the nature of the products that are formed by oxidation are determined to a considerable degree by the hydrocarbon composition of the fuel. Of the saturated hydrocarbons, the most susceptible to oxidation are naphthenoaromatic hydrocarbons, particularly tetralin and acenaphthene [1]. It must be assumed that indan is also subject to rapid and severe oxidation, and that this susceptibility to oxidation will be even greater in aromatic hydrocarbons of the indene and styrene types. Indirect evidence for the high susceptibility of styrene-type hydrocarbons to oxidation has been provided by certain analytical data on fuel oxidation products [2], which consist mostly of compounds containing a hydroxyl group attached to the side chain of monocyclic aromatic hydrocarbons with one or several double bonds. According to [3], the content of naphthenoaromatic hydrocarbons in straight-run jet fuels is, at most, 3%. These hydrocarbons are present in somewhat smaller amounts in fuels obtained by hydrogenation processes. For example, in Grade RT fuel [thermally stable jet fuel], the content of tetralins is 0.8-1.1%, and the content of indans 0.25-0.33%; in T-8V fuel, which is produced by hydrocracking vacuum gasoil, the respective contents are 1.96 and 0.61%.

It appeared desirable to determine the degree to which hydrocarbons of this type influence the oxidizability of hydrotreated fuels. For this purpose, tetralin, indan, acenaphthene, indene, styrene, and α -methylstyrene (purity 96-98%) were blended at concentrations from 0.2 to 2% in three samples of RT fuel, the characteristics of which are shown in Table 1. The blends were subjected to oxidation by 12 cycles of heating at 120°C, without any metal present; the length of each heating cycle was 6 h. The fuel sample (400 ml) was placed in a 500-ml glass flask, which was fitted with a water-cooled reflux condenser and placed in a heated air bath. At intervals during the course of the heating cycles, determinations were made of the optical density, acidity, and content of hydroperoxides in the fuel, following procedures given in [4]; at the end of the 12th heating cycle, the oxidation products in the form of adsorption resins were also determined [5].

TABLE 1. General Characteristics of RT Fuels

Indices	Source (distillates from indicated mixed crudes)		
	Volga (Sample 1)	Zhirmovsk and Korobid (Sample 2)	Orenburg, Kuibyshev, and West Siberian (Sample 3)
Density, kg/m ³	778,0	787,5	779,1
Distillation range, °C	143-229	142-243	145-225
Iodine No., g I ₂ /100 g	0,25	0,31	0,23
Acidity, mg KOH/100 ml	0,57	0,53	0,58
Content aromatic hydrocarbons, %	17,1	10,9	17,3
sulfur, %	0,01	0,005	0,008
hydroperoxides, 10 ⁴ moles O ₂ /liter	2,1	1,8	2,6
adsorp. resins, mg/100 ml			
methanol	12	8	12
acetic acid	9	6	6

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TABLE 2. Effects of Hydrocarbons Containing Aromatic Ring on Oxidizability of RT Fuel (Sample 1)

RT fuel	Content of hydroperoxides, 10^4 moles O_2 /liter				Acidity, mg KOH/100 ml				Optical density				Content of adsorption resins, mg/100 ml	
	18 h	30 h	48 h	72 h	18 h	30 h	48 h	72 h	18 h	30 h	48 h	72 h	methanol	acetic acid
Original*	37,5	48,8	53,8	55,9	1,8	3,9	6,7	16,0	0	0,11	0,23	0,34	562	98
With tetralin														
0,2%	26,3	47,5	62,5	84,1	1,5	3,6	6,6	16,8	0,01	0,15	0,21	0,36	568	—
0,5%	32,5	49,4	60,0	41,3	2,4	4,8	8,4	20,4	0,02	0,16	0,30	0,54	629	102
2%	41,3	47,5	40,0	50,0	3,6	7,0	11,5	30,2	0,10	0,26	0,50	0,93	788	—
With acenaphthene														
0,2%	23,0	48,1	60,5	75,0	1,6	3,7	6,8	15,6	0,09	0,15	0,24	0,41	614	109
0,5%	31,3	62,5	87,5	105,0	2,5	3,9	8,3	18,2	0,07	0,18	0,38	0,69	788	126
2%	46,9	80,0	97,5	100,0	2,6	4,9	10,2	28,8	0,08	0,29	0,66	1,18	903	—
With indan														
0,2%	29,6	41,9	62,5	100,0	3,3	5,3	11,1	19,7	0,16	0,20	0,34	0,78	780	452
0,5%	48,1		104,4	112,5	4,4	6,8	14,6	26,7	0,21	0,31	0,41	0,82	1200	242
With indene														
0,2%	25,3	25,9	44,6	48,8	3,1	6,8	12,3	20,2	0,15	0,21	0,42	0,89	670	160
0,5%	19,0	23,7	34,0	37,5	4,2	9,6	17,1	28,8	0,19	0,48	0,76	1,13	800	191
With styrene														
0,2%	21,8	36,3	50,9	62,1	1,9	3,4	7,2	15,3	0,06	0,10	0,15	0,22	—	—
0,5%	26,4	35,5	51,3	58,1	1,9	3,6	8,2	16,8	—	0,08	0,15	0,21	534	52
With 0,5% α -methylstyrene	29,6	38,5	43,1	31,3	2,3	3,9	9,6	17,3	0,02	0,07	0,24	0,41	751	135

* Original fuel contained hydroperoxides in amount of $2.1 \cdot 10^{-4}$ mole O_2 /liter, 12 mg/100 ml of adsorption resins desorbed by methanol, and 9 mg/100 resins desorbed by acetic acid; the fuel acidity was 0.57 mg KOH/100 ml, optical density zero.

The data illustrating the effects of these hydrocarbons on the oxidizability of the RT fuel samples (Tables 2 and 3) show that the effects depend on both the structure and character of the oxidation products. The oxidation of the No. 1 original fuel sample forms a moderate quantity of hydroperoxides ($55.9 \cdot 10^{-4}$ mole O_2 /liter) after the 12 heating cycles at 120°C ; at this time, the optical density of the fuel was 0.34, and the total content of adsorption resins 660 mg/100 ml. The No. 2 fuel sample, after the 12 heating cycles at 120°C , contained only $21.3 \cdot 10^{-4}$ mole O_2 /liter of hydroperoxides, and the total content of adsorption resins was 414 mg/100 ml. The optical density was 0.48, having shown a drop in the earlier stages of heating and a subsequent increase, with deposition of insoluble gum on the walls of the flask (1.8 mg/100 ml). The oxidation of the No. 3 fuel sample at 120°C gave a sharp increase in the hydroperoxide content, which reached $251.8 \cdot 10^{-4}$ mole O_2 /liter after the 12th heating cycle. However, this fuel formed a comparatively small amount of oxidation products as determined in the form of adsorption resins (223 mg/100 ml), and the optical density was only 0.1.

The α -methylstyrene and particularly the styrene showed the least effect on the oxidizability of the No. 1 fuel, despite the fact that these hydrocarbons have a double bond in a side chain attached to the benzene ring. The addition of 0.2 or 0.5% styrene to the fuel even gave a slight reduction in the hydroperoxide content in the initial stage of oxidation [in comparison with the results on the fuel without styrene], and only after the 8th heating cycle did the hydroperoxide content of the styrene blends approach that of the straight fuel (after the 8th cycle); the styrene blends gave somewhat higher peroxide contents upon further oxidation. However, this did not have any significant effect on the contents of products of more severe oxidation in the fuels, referring here to methanol and acetic acid resins, acidic compounds, and high-molecular-weight colored compounds. With the exception of the acidity of the fuel containing 0.5% styrene, the quantity of other oxidation products formed in this fuel, as well as the quantity of all oxidation products in the fuel with 0.2% styrene, were less than in the corresponding samples of straight fuel without styrene. In the case of the fuel blend with 0.5% α -methylstyrene, the hydroperoxide formation was slower than in the original fuel. After the 8th heating cycle, the hydroperoxide content reached a maximum, after which hydroperoxide decomposition prevailed over hydroperoxide formation, so that the quantities of the more highly oxidized products (adsorption resins, acidic compounds, and high-molecular-weight colored compounds) showed increases.

The naphthenoaromatic hydrocarbons had more severe effects on fuel oxidizability than those shown by styrene; this was particularly true of indene, which has a double bond in the naphthene ring. With only 0.2% indene in the No. 1 fuel sample, the quantities of highly oxidized products in this fuel were found to increase.

TABLE 3. Effect of Tetralin and Acenaphthene on Oxidizability of RT Fuel

Indices	Sample 2		Sample 3				
	original	with 2% tetralin	before deresining			after deresining	
			original	with 2% tetralin	with 2% acenaph- thene	original	with 2% acenaph- thene
<u>Before heating</u>							
Optical density	0	0	0	0	0	0	0
Hydroperoxide content, 10 ⁴ moles O ₂ /liter	1.8	1.9	2.5	2.8	2.6	1.1	0.9
Acidity, mg KOH/100 ml	0.56	0.56	0.58	0.58	0.58	0	0
Content of adsorption resins, mg/100 ml							
methanol	8.0	8.0	12.0	12.0	12.0	0	0
acetic acid	6.0	6.0	6.0	6.0	6.0	0	0
<u>After 3rd heating cycle (18 h)</u>							
Optical density	0.035	0.035	0	9	0.04	0	0.04
Hydroperoxide content, 10 ⁴ moles O ₂ /liter	9.0	6.0	75.0	60.0	94.6	59.4	85.3
Acidity, mg KOH/100 ml	1.4	6.0	1.1	1.3	3.9	2.1	2.8
<u>After 5th heating cycle (30 h)</u>							
Optical density	0.18	0.78	0	0.01	0.17	0	0.13
Hydroperoxide content, 10 ⁴ moles O ₂ /liter	12.5	5.4	96.8	88.3	101.9	93.7	85.3
Acidity, mg KOH/100 ml	2.9	8.6	2.5	2.9	6.4	3.7	6.9
<u>After 8th heating cycle (48 h)</u>							
Optical density	0.18	1.3	0.05	0.06	0.55	0	0.32
Hydroperoxide content, 10 ⁴ moles O ₂ /liter	15.3	13.4	141.9	112.5	150	115.5	90.25
Acidity, mg KOH/100 ml	6.9	10.9	7.5	7.0	16.0	9.9	9.6
<u>After 12th heating cycle (72 h)</u>							
Optical density	0.48	1.33	0.1	0.12	1.45	0.07	0.96
Hydroperoxide content, 10 ⁴ moles O ₂ /liter	21.3	13.8	251.8	125	207.5	160	116.3
Acidity, mg KOH/100 ml	11.7	16.6	16.3	16.3	26.8	22.6	20.35
Content of adsorption resins, mg/100 ml							
methanol	331	301	177	203	185	534	509
acetic acid	83	68	46	53	115	28.5	59

There were particularly large increases in the content of high-molecular-weight colored products; the optical density of the fuel containing 0.2% indene after the 12th heating cycle at 120°C was 0.89, in comparison with 0.34 for the fuel without indene. An increase in the fuel's indene content to 0.5% led to still lower contents of hydroperoxides and still more rapid increases in the formation of neutral and acidic products of hydroperoxide decomposition, accompanied by condensation and polymerization of the oxidation products. The fuel acidity after the 12th heating cycle was 28.8 mg KOH/100 ml, optical density 1.13, and contents of methanol and acetic acid resins 800 and 191 mg/100 ml respectively. Apparently, this strong influence of indene on the character of fuel oxidation is the result of its ready ability (in contrast to styrenes) to form low-stability hydroperoxides that decompose rapidly to form more stable compounds that are subject to further oxidation.

Indan, the same as indene, when added to the number 1 fuel in a concentration of 0.2 or 0.5%, intensified (to a somewhat lower degree) the formation of acidic and colored products, even in the initial stage of oxidation. In the presence of indan, however, there was also a substantial increase in the quantity of hydroperoxides. Only in the initial stage of oxidation of the 0.2% indan blend did we find somewhat lower hydroperoxide contents. Since the presence of 0.2% and particularly 0.5% indan in the fuel intensifies the formation of not only acidic and colored products but also adsorption resins, particularly the methanol-desorbed resins, we can postulate the formation of low-stability hydroperoxides, but at a higher rate than in the oxidation of indene.

The effects of tetralin and acenaphthene on fuel oxidizability were investigated with three samples of fuels differing in quantity and nature of the oxidation products. When either the tetralin or acenaphthene was added to fuel sample No. 1, the formation of oxidation products was found to depend on the concentration of the hydrocarbon. However, the neutral, acidic, and colored macromolecular products of oxidation in the presence of either tetralin or acenaphthene were formed in smaller amounts than in the presence of indan or indene. After the 3rd heating cycle, the presence of 0.2% of acenaphthene or tetralin in the fuel brought about a reduction in the content of hydroperoxides, as well as a somewhat lower acidity. However, as the oxidation proceeded further, the quantity of hydroperoxides with this concentration of naphthenoaromatic hydrocarbon was found to increase more rapidly than without the hydrocarbon; even so, after the 12th cycle, the fuel with the added naphthenoaromatic hydrocarbon was little different from the comparable sample of original fuel with respect to contents of other oxidation products.

When the concentration of acenaphthene or tetralin was increased from 0.2 to 0.5%, the hydroperoxide content was lower than in the straight fuel during the initial stage of oxidation; when the concentration of either hydrocarbon was increased to 2%, fuel oxidation was accelerated. With 0.5 or 2% tetralin in the fuel, the variation in hydroperoxide content during the course of the test was extremal in nature; with 0.5% tetralin, the maximal hydroperoxide content was reached after the 8th heating cycle, and with 2% tetralin the first maximum was reached after the 5th cycle. With acenaphthene, the fuel oxidation formed more hydroperoxides than when tetralin was present, and the variation in hydroperoxide content during the 12 heating cycles was nonextremal. With the acenaphthene, more high-molecular-weight colored products and methanol-desorbed adsorption resins were formed; with the tetralin, a somewhat greater amount of acidic products was formed.

The acenaphthene and tetralin differed rather markedly in their effects on fuel oxidizability (see Table 3). For example, with 2% tetralin in the No. 3 fuel, we found considerably lower hydroperoxide contents during the entire 12 cycles of heating at 120°C, with practically no effect on the rate of formation of acidic and colored products. The tetralin gave increases only in the amount of neutral oxidation products as determined in the form of adsorption resins. In contrast, with 2% acenaphthene in the fuel, we found higher hydroperoxide contents after cycles 3, 5, and 8, and this was accompanied by rapid accumulation of acidic and high-molecular-weight colored products of oxidation. As a result, the fuel acidity rose to the level of 16 mg KOH/100 ml, and the optical density to 0.55; the comparative values for the fuel without acenaphthene after cycle 8 were 7.5 mg KOH/100 ml and 0.05.

During the subsequent oxidation of the fuel containing 2% acenaphthene, hydroperoxides were not formed to the extent that they were in the fuel without the acenaphthene, but the optical density and acidity continued to increase sharply, reaching respective values of 1.45 and 26.8 mg KOH/100 ml after cycle 12. The fuel containing acenaphthene also had a higher content of adsorption resins, particularly those desorbed by acetic acid. It is suggested that such a very marked effect of acenaphthene on fuel oxidizability, i.e., the rapid formation of hydroperoxides, is due to the higher reactivity of acenaphthene, initiated by hydroperoxides.

When 2% tetralin was added to the No. 2 fuel, smaller contents of hydroperoxides were observed during the course of oxidation, and also smaller amounts of oxidation products as determined in the form of adsorption resins. However, the amounts of acidic products and the higher-molecular-weight colored products were greater with the tetralin. These colored products were measured in terms of the optical density of the fuel. With 2% tetralin in the No. 3 fuel, the optical density after cycle 12 had increased only by 0.02 (from 0.1 to 0.12); the corresponding increase for the No. 1 fuel with 2% tetralin was from 0.34 to 0.93, and for the No. 2 fuel from 0.48* to 1.33. These data indicate that heteroorganic compounds present in the fuel may interact with tetralin oxidation products.

The formation of high-molecular-weight colored products and precipitated material during fuel oxidation is due primarily to the presence of heteroorganic compounds in the fuels [6]. Hence, when these com-

* In the course of oxidation, insoluble gum is formed on the bottom and walls of the flask. In this case, the optical density decreases and subsequently increases.

pounds are removed by deresining, the oxidation of the fuel does not usually result in the accumulation of products giving a change in optical density [7]. However, as we had demonstrated previously, in the oxidation of deresined T-6 and T-8 fuels in 8 or 12 cycles of heating at 100 or 120°C, colored products are formed, despite the deresining operation [8]. Therefore, on the basis of the data we have presented here, it may be assumed that the formation of colored products in the oxidation of deresined fuels is caused primarily by the presence of naphthenoaromatic hydrocarbons. To check this hypothesis, we added 2% acenaphthene to a deresined No. 3 fuel. This particular fuel was chosen because the original No. 3 fuel gave only a small amount of colored products upon oxidation, and the addition of 2% acenaphthene gave a very sharp increase in formation of colored products. When 2% acenaphthene was added to the deresined fuel (which was free of heteroorganic compounds), the oxidation did give colored products, although in smaller amounts than when the heteroorganic compounds were present.

From the data we have presented here, it can be seen that both saturated and unsaturated naphthenoaromatic hydrocarbons have substantial effects on the oxidizability of fuels obtained by the use of hydrogenation processes.

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