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Study of Radiation Effect on Petroleum Oils

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Research Article

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Abstract

The article provides the gas chromatographic results of decomposition products produced by radiation of the low-viscosity hydraulic oils. The analysis of radiation effect of different doses on model mixtures distinguishing by hydrocarbon composition allowed establishing that hydrogen and hydrocarbon gases are the main components of the hydrocarbon radiation decomposition. The cycloalkane hydrocarbons subjected to dehydrogenation are the main hydrogen source under radiation exposure. The alkanes of different branching degree and alkane substituents of cycloalkanes serve as the hydrocarbon gas source. The arene structures have a stabilizing effect on the hydrocarbons regard to the radiation. It was shown that isoparaffinic hydrocarbons demonstrate the least degradation under action of radiation. The stabilizing effect of monocyclic aromatic hydrocarbons with branched alkyl substituents was confirmed.

Keywords: Hydrocarbon; Gas; Cycloalkanes; Fluids; Radiation; Chromatography

Introduction

A necessity to evaluate the thermal stability of the product or its hydrocarbon constituents as well as its oxidation or radiation stability almost always arises in the development or use of new grades industrial oils, hydraulic fluids and synthetic products of special purpose depending on their operational conditions. The following conditions are regarded as essential for this evaluation: scientific validity, reliability of results, rapid determination procedure and strictly limited volume of the sample, which are often obtained on the pilot plant or from the liquid-adsorptive separation.

The laboratory unit has been developed and installed in order to evaluate the volatility, thermal and thermo-oxidative stability of high-dearomatized low-viscosity products boiled out within 260–280°C, 200–340°C. Its principle operation is based on hybrid combination of thermal analysis and reaction gas chromatography methods which allow recording the sample weight loss over time without any special weighing device [1].

The radiation effect on different hydrocarbon groups in the development of new-generation petroleum low-viscosity hydraulic oils for the rocket and space technology management system produced from large-scale domestic oils applying hydrocatalytic processes has been studied. The radiation stability is considered to be one of the main performance characteristics for this oil group due to their specific application [2].

The analysis of radiation decomposition gaseous products by gas chromatography method has been developed to evaluate radiation stability and gas release of existing and newly developed low-viscosity hydrocarbon bases and hydraulic fluids. The study comprises the following steps: sample preparation, its irradiation and analysis of the radiolysis gaseous products.

Sample preparation consists of deaeration of the sample weighed on the counter-balance with accuracy up to 0.01 g and put in a special glass ampule (L = 0.350 m; d = 0.025 m) followed by its sealing.

The deaeration has been performed by repeated (3–4 times) liquid nitrogen freezing of the sample under vacuum not lower than 1–2 mm Hg. Upon completion of degassing the ampule was sealed.

The irradiation has been performed with Co^{60} on the facility of the Electrochemistry Institute of the Russian Academy of Sciences till total dose from $1 \cdot 10^6$ to $1 \cdot 10^8$ rad, with dose rate of 355 rad/s.

Methods

A special design sampler has been developed to open the ampule. This design permits extracting gaseous products of the hydraulic fluid radiation decomposition from the sealed ampule without risk of releasing decomposed products into atmosphere. This opportunity has been realized by breaking the ampule inside the sealed sampler (Figure 1). The sampler design permits to select the gaseous phase with an injection syringe.

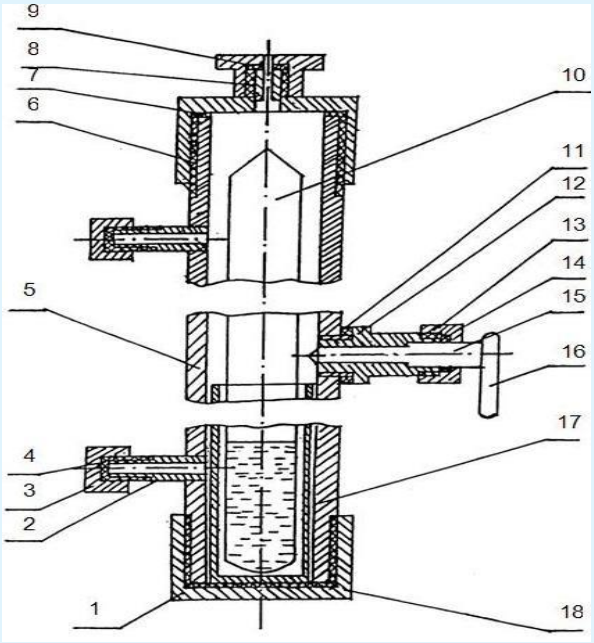


Figure 1: The sampler for gas chromatography analysis of radiolytic decomposition gases of hydraulic fluids:1 –cover; 2 –inert gas fitting; 3 –cover; 4,7,11,14,18 –rubber spacers; 5 –body; 6 –fitting; 8, 13 –screw; 9 –rubber diaphragm; 10 –ampule; 12 –flange; 15 –rod screw; 16 –lever; 17 –glass.

The Head Space Analysts method has been adopted for the gas chromatography analysis of the hydraulic fluids radiation decomposition gaseous products [3]. The preliminary tests results revealed that the room temperature of 20–25 ˚C can be considered as optimum conditions for the phase equilibration throughout the sampler. Strict adherence to all analysis conditions allows using direct analysis results as assessment criteria of test samples radiation stability.

The chromatographic system composed of two parallel systems, sample injector-column-detector-potentiometer (Figure 2) has been mounted for more effective use of chromatographic devices for analysis of low-viscosity oil radiation decomposition gases. This system provides use of a column with 5 Å molecular sieves connected to the thermal conductivity detector (TCD) for hydrogen analysis and aluminium oxide column modified with

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vaseline oil connected to the flame-ionization detector (FID) for C_1-C_4 analysis.

The chromatographic system principal diagram is given in Figure 2. The system equipment with additional recorder (potentiometer) allows recording simultaneously signals obtained from each detector to form the chromatogram.

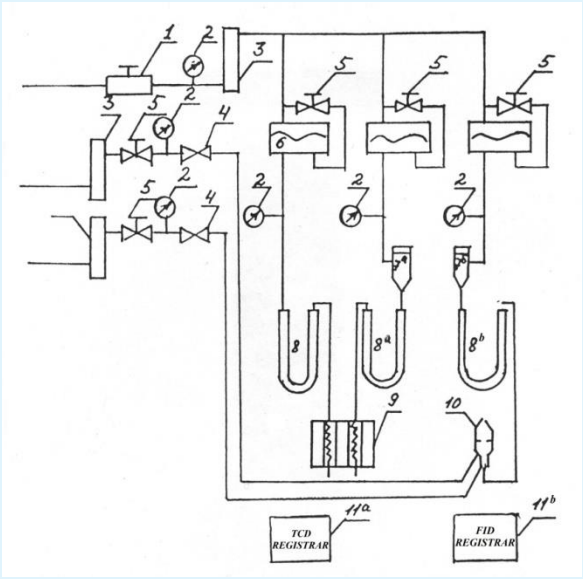


Figure 2: Chromatographic system principal diagram: 1 –pressure regulator; 2 - manometer; 3 – dehydrators; 4 - metering valves; 5 –gas flow adjustment valves; 6 –flow control valve; 7a,7b–fore column-ample injector; 8 –reference column, 8a – working column with 5 Å molecular sieves,8b – working column (aluminium oxide+15 % vaseline oil); 9 –thermal conductivity detector; 10 –flame-ionization detector; 11a,11b– potentiometers

The temperature of the common column thermostat was kept at a level of 55°C. Chromatogram of C_1-C_4 hydrocarbons is given in Figure 3. Quantitative interpretation was performed by the absolute calibration method. Metrological characteristic of repeatability was the main accuracy factor of the method.

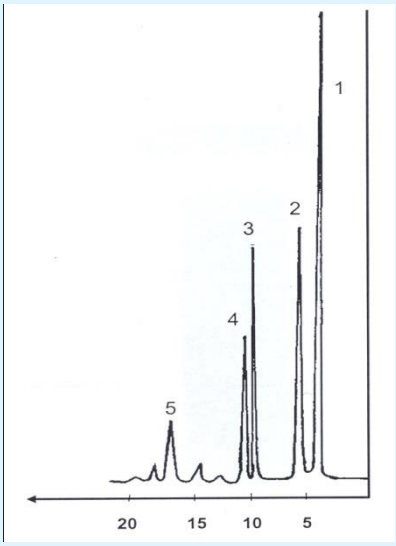


Figure 3: Chromatogram of C_1-C_4 hydrocarbons:1 – methane, 2 –C_2 hydrocarbons, 3 –propane, 4 – propylene, 5 - C_4 hydrocarbons.

Results

The repeatability value has been calculated according to the applicable requirements. 4 samples of hydraulic fluids exposed to radiation effect of different degrees were used as study subjects. Five sequential analyses (n_i) of each sample have been performed. Number of degrees of freedom amounted to 20. Results of statistical processing of result analysis are given in Table 1.

Radiation dose, rad	Component	Component Content, % vol.					x	S_i	r
		Sequential Tests							
		1	2	3	4	5			
$1\cdot10^8$	H_2	14.7	14.4	14.0	13.6	13.2	14.0	0.51	2.0
	CH_2	0.1248	0.1238	0.1226	0.1215	0.1200	0.1225	0.0020	0.008
	$\sum C_2$	0.2012	0.1950	0.1902	0.1890	0.1834	0.1918	0.0068	0.025
	C_3H_8	0.0780	0.0751	0.0725	0.0714	0.0690	0.0732	0.0034	0.014
	C_3H_6	0.0808	0.0800	0.0796	0.0709	0.0788	0.0796	0.0009	0.004
	$\sum C_4$	0.0800	0.0770	0.0752	0.0734	0.0720	0.0755	0.0034	0.014
$1\cdot10^7$	H_2	5.10	4.90	4.70	4.60	4.60	4.80	0.22	0.86

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	CH_2	0.0844	0.0831	0.0808	0.0793	0.0782	0.0812	0.0027	0.011
	$\sum C_2$	0.0556	0.0552	0.0526	0.0496	0.0476	0.0521	0.0036	0.015
	C_3H_8	0.0180	0.0172	0.0166	0.0161	0.0156	0.0167	0.0010	0.004
	C_3H_6	0.0247	0.0240	0.0232	0.0229	0.0226	0.0235	0.0010	0.004
	$\sum C_4$	0.0170	0.0168	0.0166	0.0160	0.0155	0.0164	0.0006	0.002
$5 \cdot 10^6$	H_2	0.84	0.80	0.75	0.72	0.70	0.76	0.05	0.20
	CH_2	0.0120	0.0115	0.0112	0.0010	0.0095	0.0090	0.0028	0.011
	$\sum C_2$	0.0080	0.0076	0.0074	0.0072	0.0070	0.0074	0.0004	0.002
	C_3H_8	0.0020	0.0019	0.0018	0.0018	0.0017	0.0018	0.0002	0.001
	C_3H_6	0.0030	0.0028	0.0027	0.0026	0.0025	0.0027	0.0002	0.001
	$\sum C_4$	0.0020	0.0019	0.0017	0.0017	0.0016	0.0018	0.0002	0.001
$1 \cdot 10^6$	H_2	0.2288	0.2265	0.2242	0.2200	0.2190	0.2237	0.0042	0.016
	CH_2	0.0022	0.0020	0.0018	0.0017	0.0016	0.0019	0.0002	0.001
	$\sum C_2$	0.0015	0.0014	0.0013	0.0013	0.0012	0.0013	0.0001	0.0005
	C_3H_8	0.0004	0.0004	0.0004	0.0003	0.0003	0.0004	0.0001	0.0005
	C_3H_6	0.0005	0.0005	0.0005	0.0004	0.0004	0.0005	0.001	0.0005
	$\sum C_4$	0.0005	0.0005	0.0005	0.0005	0.0004	0.005	0.0001	0.0005

Table 1: Calculation of repeatability

The repeatability value was defined according to the formula:

$$r = t_{0.95(ni-1)} . S_i \sqrt{2} \qquad (1)$$

Where $t_{0.95(ni-1)}$ is a Student's coefficient for (n_{i-1}) degrees of freedom with a confidence coefficient of 0.95. The gas release was calculated in cm^3 per 1 g of oil according to gas chromatography analysis data and taking into account that the sampler volume with the rest of ampule was 210 cm^3.

It was discovered by MF Romantsov [4] that arenes are the most radiation-resistant components of lubricant oils. Aromatic structures demonstrate significant advantages, when compared to other hydrocarbons in terms of resistance to destruction and gas emission [4].

An arene impact on radiolytical stability (dose $3 \cdot 10^7$ rad) of model mixtures 3, 5, 6 and 7 was studied (Table 2). Model mixtures were based on dearomatized fractions with addition of various concentrations of polyalkyl benzenes. It was established that introduction of polyalkylbenzenes (fraction 285-305°C, 10 % w/w) leads to dramatic decrease of gas emission rate (by 70% to 40%). Besides that, it was found that bases with different structural-group composition demonstrate various susceptibility to arenes. In case of models 3 and 7, mostly based on isoalkanes and with addition of polyalkylbenzenes (10% w/w), hydrogen formation rate decreased by 67% and 51%, respectively, while in the same conditions models 5 and 6, based on different condensed cycloalkanes, showed decrease of hydrogen formation rate by 42% and 40%, respectively.

Hydrocarbon Type	Model Mixtures						
	1	2	3	4	5	6	7
Alkanes of different branching degree, %	33.5	84.8	87.5	36.5	41.4	-	78.2
Cycloalkanes, %:	65.6	7.7	11.6	61.4	58.0	100.0	20.0
-mono	43.1	2.8	1.4	16.3	20.5	100.0	10.5
-bi	7.4	2.1	3.6	20.4	15.8	-	4.6
-tri	10.6	1.7	2.6	20.9	17.9	-	4.9
-tetra	4.0	1.1	2.8	3.4	1.2	-	-
-penta	0.5	-	1.2	0.4	1.9	-	-
Alkylbenzenes, %	0.9	7.5	0.9	2.1	1.8	-	0.6

Table 2: Hydrocarbon structural-group composition of model mixtures.

Stabilizing effect of arenes can be clearly seen from the quantities of methane formed depending on the radiation dose (Figure 4) for two model groups: 2, 4 and 3, 5. Said groups differ in their background: models 3 and 5 are dearomatized products of adsorptive fractionation of models 2 and 4, respectively. Models 3 and 5 (curves 1' and 2') demonstrate more intensive methane formation for almost all dose values in the range under study than models 2 and 4 (curves 1 and 2).

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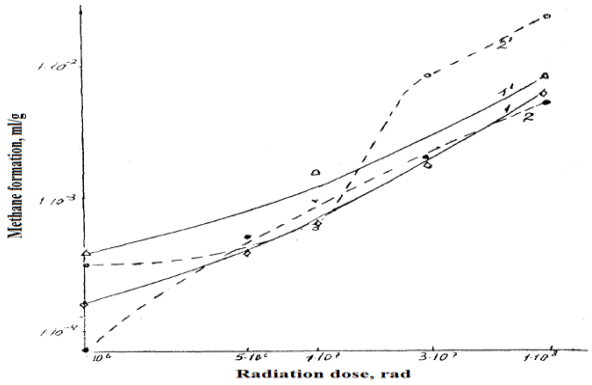


Figure 4: The effect of arene hydrocarbons on methane formation in the course of radiation.
1' – model 3; 2' – model 5; 1 – model 2; 2 – model 4

No microscopic changes in physicochemical properties and structural-group composition of hydrocarbon liquids were noticed after irradiation for all dose values in the range close to working conditions. Nevertheless, substantial composition changes of trace impurities in model hydrocarbon mixtures were revealed by thermal desorption method, depending on radiation dose. Those microscopic changes cause macroscopic processes like gas emission leading to flight control system failure.

Experimental proof of hypothesis stated above can be found in the curves depicting changes of separate hydrocarbon groups content for models 4 and 5 (Figure 5) combined with hydrogen formation (curves 4 and 4').

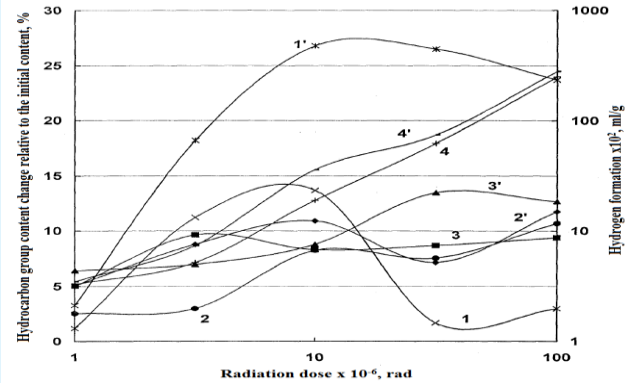


Figure 5: Effect of arene hydrocarbons on the hydrogen formation and hydrocarbon composition changes (thermal desorption) of models 4 (1', 2', 3' and 4') and 5 (1, 2, 3 and 4).
1 and 1' curves – isoalkanecontent change,
2 and 2' curves – cycloalkanecontent change,
3 and 3' curves – arenecontent change,
4 and 4' curves – hydrogen formation

Given the fact that models 3 and 5 are dearomatized derivatives of models 2 and 4, one can conclude that arenes have a stabilizing effect on all structural hydrocarbon groups (curves 1 and 1' for alkanes, curves 2 and 2' for cycloalkanes, curves 3 and 3' for arenes), leading to decrease of gas emission rate (curves 4 and 4' in Figure 5 for hydrogen emission and curves 1, 1', 2, 2' in fig. 4 for methane formation). Additionally, dependency of hydrogen and gaseous hydrocarbons formation rate on radiation dose was studied. Gas formation (H_2 and CH_4) after irradiation ($1 \cdot 10^8$ rad) of model mixtures with different cycloalkane content is shown in bar diagram (Figure 6). Given the data obtained one can conclude that cycloalkanes demonstrate the highest hydrogen emission rate (Figure 5).

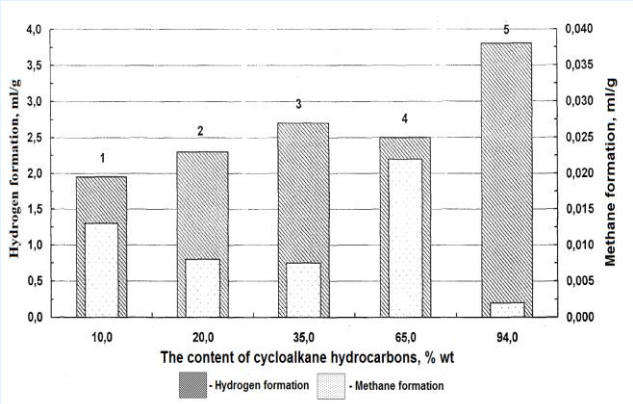


Figure 6: Hydrogen and methane formation during irradiation ($1x10^8$ rad) of models mixtures with different hydrocarbon composition. 1 – model 7; 2 – model 2;3 – model 1;4 – model 4;5 – model 6.

As it was established that such behavior is characteristic for model 6 (100% cycloalkane content) for almost all doses studied. Lower rate of gaseous hydrocarbons formation can be explained by lack of large alkyl substituents in di-(methylcyclohexyl) methane (main component of mixture 6). This fact is also true for all radiation doses under study.

Amount of gas phase, its qualitative composition and changes of liquid phase composition of hydrocarbon media result from complex chemical processes, initiated by irradiation.

The analysis of radiation effect of different doses on model mixtures distinguishing by hydrocarbon composition allowed establishing that hydrogen and hydrocarbon gases are the main components of the

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hydrocarbon radiation decomposition. The cycloalkane hydrocarbons subjected to dehydrogenation are the main hydrogen source under radiation exposure. The alkanes of different branching degree and alkane substituents of cycloalkanes serve as the hydrocarbon gas source. The arene structures have a stabilizing effect on the hydrocarbons regard to the radiation.

Taking into account that hydrogen is the main gas component of hydrocarbon radiation decomposition, based on obtained study results it can be said that the alkane structures of different branching degree are the most preferable structures of dearomatized bases of hydraulic fluids in relation to the radiation resistance to gas formation. Besides, a number of monocyclic arene structures with branched alkyl substituents can serve as stabilizers and increase the fluid radiation stability.

In such a way it was found that the isoalkane hydrocarbons are the most preferable hydrocarbons as a component of low-viscosity oils used for autonomous hydraulic power units from the point of view of antiradiation properties. This provision along with assessment of antiwear properties was taken as a basis of selection of specified hydrocarbon composition of the low-viscosity hydraulic oils produced from large-scale domestic petroleum oils applying hydrocatalytic processes for the rocket and space technology management system, equivalent of hydraulic fluids from unique Balakhany petroleum oil.

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