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THE CHEMISTRY OF ORGANIC SULFUR COMPOUNDS CONTAINED IN PETROLEUMS AND PETROLEUM PRODUCTS (SELECTED ARTICLES)

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PETROLEUMS OF THE NEW OIL SITES IN THE BASHKIR AUTONOMOUS SOVIET SOCIALIST REPUBLIC

A. S. Eigenson, Ye. G. Ivchenko, I. I. Kantor
and G. V. Sevast'yanova

The production of petroleums in the Bashkir Autonomous Socialist Soviet Republic will rise, principally because of the increase in the production of petroleums of high sulfur content. The amount of these produced in Bashkiria in 1965 will be 50% of all petroleum produced.

The high-sulfur petroleums of Bashkiria may be divided by their qualities into petroleums of the Arlanskiy and Ishimbay types. Arlanskiy-type petroleums contain 2.5-3.2% sulfur, 20-25% silica-gel and asphaltene resins. The fraction which boils away at temperature from the beginning of boiling to 200° contains 0.15-0.17% sulfur; and its octane number is 40-43. The sulfur content increases sharply in proportion to the loading of the fractional composition. In comparison with Tuymazy and Romashkinskiy petroleums those of the Arlanskiy type are heavier: their density is 0.885-0. 9 as against 0.[illegible]66 for the Romashkinskiy type; the sulfur content is 1.5 to 2 times higher in both the petroleums themselves and their distillates. South Bashkirian oils of the Ishimbay type (Tereklian and Vvedenovskiy) contain about 2% sulfur. Unlike the petroleums of the northwest regions those of the southern fields are lighter: density, 0.846-0.860; silica-gel and asphaltene resin content, 12-15%. The potential content of bright stocks is high: 27-30% of the fractions evaporating at temperatures up to 200°, 43-47% of those to 300°. The octane number of the fractions evaporating up to 200° is 45-50. The sulfur content of fractions suitable for kerosene and diesel fuel is 0.9-2%.

In connection with the continually increasing production of high-sulfur petroleums great attention is being paid to processing them: the elaboration of new layouts using processes for improving motor fuels (hydrocracking, catalytic refor..ing). The use of these processes on high-sulfur petroleums leads, of course, to increased capital outlay and working costs. A technological-economic analysis of installations for various depths of processing these petroleums has shown, however, that the construction of such works is profitable and provides completely acceptable periods of capital-outlay amortization (about three years).

We must know the trade and raw-material characteristics of the petroleums from the new fields in order to solve correctly the problems in processing these high-sulfur petroleums. In 1958 the Raw-Material Laboratory of the Bashkir Research Institute (BashNII) conducted an investigation of these characteristics for the following petroleums: Cheraul'skiy (carboniferous formation), Cheraul'skiy (Vereyskiy level), Arlanskiy (Kashirskiy level), Yugomashevskiy (Devonian), Kush-Kul'skiy (Upper Devonian, Kynovsko-Kashiyskiy strata), and Tereklian (Sakmaro-Artinskiy deposits).

Cheraul'skiy (carboniferous), Yugomashevskiy, and Kush-Kul'skiy petroleums are characterized by high density (0.885-0.895), high content of sulfuric acid resins (58-80% by volume), and high sulfur content (2.2-3.19%). Cheraul'skiy (carboniferous) and Kush-Kul'skiy petroleums are close to Arlanskiy (carboniferous) in yield of fractions evaporating at temperatures up to 200 and 300° and in distillate quality. The gasoline fractions evaporating up to 200° are characterized by a not high content of sulfur and a low octane number. Fractions suitable for diesel fuel have a higher sulfur content in comparison with GOST [All-Union (Soviet) State Standard] specifications (2.84%). The diesel-fuel fractions of Yugomashevskiy petroleum, however, contain less sulfur than similar fractions of other northwest-region petroleums. The sulfur content in these fractions nevertheless exceeds the GOST specification and further purification of the diesel-fuel fractions of all three petroleums from organic sulfur compounds would be necessary.

Arlanskiy petroleum (Kashirskiy level) differs from Arlanskiy (carboniferous formation) petroleum in a somewhat lower sulfur content (2.68%) and lesser density (0.878 against 0.893). It contains 21.4% of the fractions evaporating up to 200° and 37.7% of those evaporating up to 300%, against 18% and 31.6% for Arlanskiy (carboniferous formation) petroleum. Petroleum of the Kashirskiy level contains dissolved hydrogen sulfide; therefore even light gasoline fractions contain a considerable amount of sulfur and have low octane numbers, which essentially differentiates this petroleum from those of the carboniferous formation. Fractions of Arlanskiy (Kashirskiy level) petroleum which evaporate above 220° contain somewhat less sulfur than the corresponding fractions of Arlanskiy (carboniferous formation) petroleum. Thus, a diesel-fuel fraction evaporating within the limits of 220-350° contains 2.16% sulfur against 2.47% for petroleum of the carboniferous formation. The cetane ratings of diesel fuels are high and lie within the limits 49-55 for fuels of different fractional composition. The residues of Arlanskiy (Kashirskiy level) petroleum after separation of fractions to 300° and higher are sulfur-containing (3.63% to 4.24% sulfur); and the residues with b.p. higher than 370° are in addition also of high viscosity (nominal viscosity at 80° equals 25.3° VU. Consequently Kashirskiy level petroleum can be processed according to the system for Arlanskiy (carboniferous formation) petroleum, after having provided for supplementary cleaning of sulfur from the gasoline distillates.

Petroleum from the Cheraul'skiy deposit of the Vereyskiy level differs from the petroleum of the northwest regions of Bashkiria in its general characteristics and those of its distillates by direct fractionation. In its trade characteristics this petroleum is close to Romashkinskiy (Devonian level) petroleum. The fraction evaporating at temperatures from the beginning of boiling to 200° contains 0.1% sulfur in comparison with 0.27% in the same fraction from petroleum of the carboniferous formation. Of these fractions 59-64% are paraffin hydrocarbons and their octane numbers are low (40-55). These fractions must be aromatized and isomerized in order to raise the octane numbers. Fractions suitable for diesel fuel in fractional composition are characterized by low sulfur content (1.36% in the 200-350% fraction) in comparison with fractions of carboniferous-formation petroleum. We can obtain 8-9% of diesel fuel with a sulfur content up to 1% from Cheraul'skiy (Vereyskiy level) as well as from Romashkinskiy petroleum. Purification from sulfur is necessary in order to obtain trade diesel fuels which boil out over a wide range. Fuel oils up to GOST requirements can be obtained from the residuals of Cheraul'skiy (Vereyskiy level) petroleum. Thus this petroleum may be processed together with Romashkinskiy.

Tereklian petroleum bears a relationship to the southern petroleums of Bashkiria. In comparison with petroleums of the Ishimbay region--Ishimbay, Vvedenovsk, Starokazankov--it may be characterized as containing less sulfur and as being lighter. Hydrogen sulfide is dissolved in this petroleum; its sulfur content is 2.42%; density, 0. 46; sulfuric-acid resin content, 20%; content of fractions boiling out up to 200°, 30.7% and to 350%, 55.6%. The gasoline fractions are characterized by a high sulfur content and a low octane number. The 200° fraction contains 0.65% sulfur and has an octane number of 45.2. Hydrocracking of the pertinent fractions is necessary for the obtention of trade gasolines from Tereklian petroleum and aromatization is necessary for raising its octane characteristics. Fractions suitable for kerosene and diesel fuel are characterized by a high sulfur content. The diesel fuel fractions in addition contain dissolved sulfuric acid. The residuals after removal of fractions above 450-500° are of slight viscosity. For obtaining trade fuels when processing Tereklian petroleum the system is applicable which was proposed for high-sulfur petroleums of the northwest regions.

Conclusions

1. All the investigated petroleums of Bashkiria can be divided into three groups depending on the distribution of sulfur through their fractions:

a) petroleums with a not high sulfur content in the gasoline fractions (not more than 0.1%) which gradually and uniformly increases in the kerosene and diesel fuel fractions;

b) petroleums with a not high sulfur content in the gasoline fractions which increases sharply in the kerosene and diesel fractions;

c) petroleums in which the gasoline fractions contain a considerable amount of sulfur (0.5% and above) and in the kerosene and diesel fuel fractions of which the sulfur content correspondingly in eases.

2. Fuels in accordance with GOST specifications may be obtained from petroleums of the first group without purification. Only asoline fractions may be obtained from the second group without speci purification. All the fuels from the third group require ification.

THERMAL STABILITY AND CORROSIVENESS OF SULFUR FUELS AT HIGH TEMPERATURE

Ye. R. Tereshchenko, et al.

Because of the increase in the temperature in engine fuel systems, the study of the thermal stability and corrosiveness of fuels at high temperatures acquires great practical significance. This problem arises particularly in connection with sulfur fuels, which usually contain corrosive sulfur compounds along with low-stability components.

Presented in this paper are the results of investigations conducted in 1958-1959 on the study of thermal stability and corrosiveness in fuels obtained from eastern petroleums.

The following fuels were subjected to the investigations: TS-1 standard, TS-1 subjected to hydropurification, TS-1 with an increased mercaptan content, and T-2 type fuel with a wide fractional composition containing thermal-cracking components.

The physicochemical properties of the investigated fuels are given in Table 1.

The thermal stability and corrosiveness of the sulfur fuels were studied under static conditions in a bomb and under conditions of pumping the fuel through a filter in an actual engine fuel system.

TABLE 1

Physicochemical Properties of Investigated Fuels

Fuel	Density at 20°C	Boiling range °C	Sulfur content, %	Mercaptan content, %	Iodine number, g of iodine per 100 g of fuel	Content of actual tars, mg per 100 ml of fuel
TS-1 standard	0.777	133-230	0.066	0.009	2.55	4.40
TS-1 hydropurified	0.777	142-234	0.015	None	1.00	None
TS-1 with increased mercaptan content	0.778	138-240	0.17	0.032	3.40	3.60
T-2 type with thermal cracking components ...	0.765	72-248	0.23	0.008	23.00	9.60

Test in Bomb

The fuel (100 ml), which had been previously filtered through a paper filter, was poured into a glass beaker, which was then placed in the bomb. The bomb test was conducted at 150°C with a four-hour duration. After the test the fuel was cooled to room temperature and then filtered through a paper filter. The sediment in the filter was washed with isopentane, after which the filter with the sediment was brought down to a constant weight in a thermostat at 100-105°.

The thermal stability of the fuel was estimated according to the amount of sediment formed per 100 ml of fuel, while the corrosiveness was estimated on the basis of the loss in the weight of bronze plates during the test. The plates were made from the bronze that is used in the production of parts for the fuel systems of engines. The results of the investigation of the stability and corrosiveness of fuels by the above-described method are given in Table 2.

From the data listed in Table 2 it is apparent that of the fuels investigated the TS-1 subjected to hydropurification possesses the best thermal stability.

TABLE 2

Stability and Corrosiveness of Fuels

Fuel	Amount of precipitate, mg/100 ml		Tar content, mg/100 ml		Acidity, mg KOH/100 ml		Weight losses in bronze plates, g/m²
	Without metal	With bronze	Without metal	With bronze	Without metal	With bronze	
TS-1 standard...........	5.3	18.5	11.2	14.8	2.85	3.09	1.49
TS-1 hydropurified ...	1.0	7.2	7-2	10.8	4.92	5.60	0.50
TS-1 with increased mercaptan content	4.9	32.5	18.8	17.4	2.77	4.50	3.32
T-2 type with thermal cracking components ..	21.3	34.5	38.0	50.2	6.8	3.88	None

As was to be expected, the formation of tars in the T-2 type fuel containing cracking components proceeded with greater intensity than in the direct-distillation fuels, which do not contain thermal-cracking components.

Our attention is drawn to the fact that when testing in contact with bronze the amount of sediment in the direct-distillation sulfur fuels is approximately 3-7 times greater than when testing without bronze, while in the case of the T-2 sulfur fuel containing cracking components the effect of the bronze on sedimentation is exhibited much more weakly. This attests to the fact that the formation of insoluble precipitates in the former case occurs mainly as a result of the precipitation of the products of the corrosion of the bronze, while in the second case the sedimentation is due (primarily) to the oxidation of various fuel compounds and their settling out as a solid phase.

The T-2 type fuel causes practically no corrosion of the bronze. The hydropurified TS-1 fuel possesses insignificant corrosiveness in comparison with the standard TS-1.

Test on a Miniature Apparatus

The apparatus used in the fuel tests to simulate the operation of a fuel filter consisted of the following basic parts: a fuel tank, a pump, a coil-type preheater, a filter, a cooler, an overflow tank, and an instrumentation system. At a definite set regime the fuel was pumped through the preheater and filter and the change in the resistance of the filter was determined as a function of the test time. The following regime was used in the tests: the pressure of the fuel before the filter was kept constant and equal to 3 kg/cm^2; the pumping rate of the fuel through the filter was 3.6 liters/hr per cm^2; a bronze sieve was used as the filter.

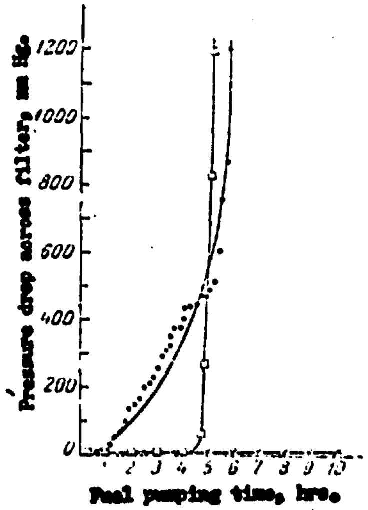

Fig. 1. Variation in the pressure drop across the sieve filter as a function of the pumping time in sulfur fuels at 120°C. □) T-2 type fuel containing thermal-cracking components; ●) TS-1 fuel with increased mercaptan content; x) TS-1 standard.

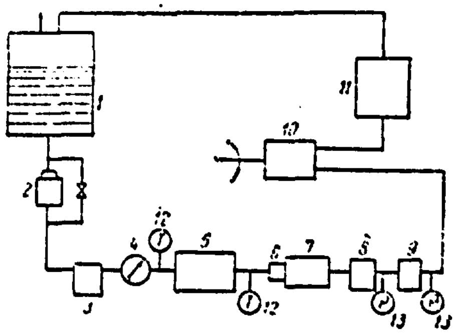

Fig. 2. Diagram of apparatus with actual fuel units. 1) fuel tank; 2) booster pump; 3) sieve filter; 4) flowmeter; 5) heat exchanger; 6) holder with metal plates; 7) radiator; 8) filter; 9) paper filter; 10) fuel unit; 11) cooler; 12) thermocouple; 13) manometer.

The tests were conducted under conditions of single-cycle pumping of the fuel through a tube in contact with bronze metal plates installed in front of the filter. The criterion for estimating the thermal stability of the fuels was the rate at which the filter was clogged with sediment, this rate being characterized by the pressure drop across the filter.

The corrosiveness of the fuels was estimated on the basis of the change in the weight of the plates during the time of the test.

The results of the fuel tests are presented in Fig. 1. As is apparent from Fig. 1, TS-1 with increased mercaptan content and T-2 type with cracking components proved practically the same with respect to the rate of clogging of the filter (50-60 μ bronze sieve). These fuels possess an extremely low thermal stability and cause rapid filter clogging.

TS-1 standard has a considerably lesser tendency to deposit insoluble precipitates on the filter. The results obtained agree with the results of evaluations of fuels tested in the bomb.

Listed below are the results of an estimate of the corrosiveness of the fuels using the pumping apparatus at 120°C and for a test duration of 5 hr - 5 hr and 40 min. (losses in weight of bronze plates, g/m²):

TS-1 standard	4.26
TS-1 with increased mercaptan content	8.80
T-2 type fuel with thermal-cracking components	0.98

It is apparent from these data that T-2 type fuel containing thermal-cracking products causes insignificant corrosion of bronze. Of all the fuels tested TS-1 with increased mercaptan content (0.032%) possesses the highest corrosiveness.

Test on an Apparatus with Actual Fuel Units

A diagram of the apparatus appears in Fig. 2.

The following testing regime was used: the fuel pressure before the sieve and paper filters 2.5—3 kg/cm²; rate of fuel flow 2300—2400 liters/hr; temperature of fuel in tank 15—25°; in the preheater the fuel was heated to a temperature established by the testing regime.

The fuel was pumped through a closed circuit.

The test was continued until the paper filter was clogged to the point where the pressure drop across it rose to 0.8 kg/cm², but for not more than 10 hrs. The 10-hour tests were conducted in three stages: 2 for 4 hours each, and 1 for 2 hrs.—with a fuel change after each stage. The stability of the fuels was estimated on the basis of the rate of clogging of the paper filter.

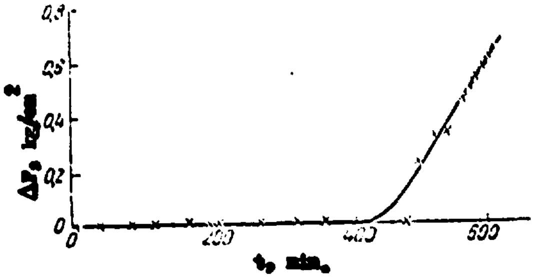

Fig. 3. Variation in the pressure drop across the paper filter as a function of the pumping time for TC-1 with increased mercaptan content at 120°C.

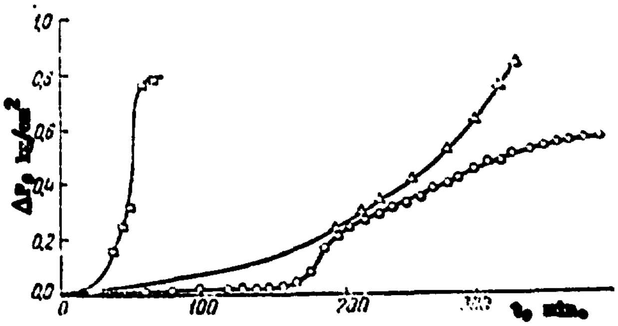

Fig. 4. Variation in the pressure drop across the paper filter as a function of the pumping time for T-2 type fuel containing thermal-cracking components at different temperatures.

Data characterizing the tendency of TS-1 fuel with increased mercaptan content and T-2 type fuel containing thermal-cracking components to deposit insoluble precipitates on a full-scale paper filter are presented in Figs. 3 and 4. The data given show that these fuels possess low thermal stability at the temperatures tested and cause rapid filter clogging.

After the test of each fuel the paper filter and the pump parts were submitted to visual examination. On the filter and parts of the units dark brown resinous deposits were observed.

Conclusions

1. Of the investigated fuels, obtained from sulfur petroleums, the lowest thermal stability at 120° was found for fuels containing thermal-cracking components and an increased quantity of mercaptans (these latter form a large quantity of insoluble sediments and tars). Pumping these fuels at the stated temperature caused rapid clogging of the filters and was attended by the formation of deposits on the parts of the fuel units.

2. Corrosiveness of the fuels with respect to bronze depends mainly on the presence of mercaptans in the fuel. T-2 type fuel, which contains thermal-cracking components, possesses low corrosiveness.

3. The use of hydropurification in the production of TS-1 type fuels permits a significant increase in the thermal stability and a reduction in the corrosiveness of the fuels obtained from eastern petroleums.

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