Comparative analysis of oil properties from Western Siberia oil fields

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Abstract. The article provides a comparative analysis of oil properties from Western Siberia fields. Experimental data on fractional composition, oil density, sulphur content, chloride concentration, kinematic viscosity, water content are shown, which proves the quality of oil produced, which is important for both producers and consumers of oil, including Russian and foreign enterprises.

1. Introduction
The strategy of Russia's development in the field of power engineering provides for an increase in the volume of oil refining up to 220-225 million tons per year. A significant part of the obtained oil products is planned to be exported, including to Western Europe. However, the continual tightening of environmental and quality requirements of the European Union to consumed petroleum products may lead to a reduction in export opportunities for the Russian oil refining industry.

Due to this, the task of ensuring a world-class level of quality of products is becoming increasingly relevant for domestic refineries. The complexity of its solution is largely determined by the quality of raw materials coming in for processing. Consequently, determination of the quality of oil extracted from various deposits on the territory of the country acquires great significance both for producers and consumers of oil [1].

Of course, oil is a mutual conjugate solution of hydrocarbons and heteroatomic organic compounds. Oil as a dispersed system is a complex, multicomponent, inter-soluble mixture of gaseous, liquid and solid hydrocarbons of different chemical structure with the number of carbon atoms up to 100 or more with an admixture of heteroorganic compounds of sulphur, nitrogen, oxygen and some metals. It's not a secret that the chemical composition of oil from various fields is very diverse. The elemental composition of oil is the least variable: 82.5 - 87% carbon; 11.5 - 14.5% hydrogen; 0.05 - 0.35, rarely up to 0.7%, oxygen; up to 1.8% nitrogen and up to 5.3%, rarely up to 10%, sulphur. In oil, metals are also found (Ca, Mg, Fe, Al, Si, V, Ni, Na, etc.). Oil consists mainly of hydrocarbons of four groups: paraffin (alkanes), naphthenic (cycloalkanes), aromatic (arenes) and hybrid - paraffin-naphthenic-aromatic. Oxygen, sulphur and nitrogen are present in the form of oxygen, sulphur and nitrogen compounds. The relative content of hydrocarbon groups in oil fractions is very different. The predominance of hydrocarbons gives different properties to oil, which inevitably affects the processing methods and the fields of application of petroleum products. Paraffin hydrocarbons - alkanes $C_nH_{2n+2}$ - are the basis of the group components of oil, the total content of which is 25-35% of the mass (not counting the dissolved gases). Alkanes of the normal structure and isoalkanes, mostly monomethyl-substituted, with different positions of the methyl group in the chain.
are most widely represented. With increasing molecular weight of oil fractions, the content of alkanes in them decreases. Naphthenic hydrocarbons - cycloalkanes (cyclanes) - are included in all fractions of oil, except gases. On average, in oils of various types, they amount to 25-80% of the mass. The distribution of naphthenic hydrocarbons by oil fractions is very diverse. Their content usually grows as the fractions become heavier. The distribution of cycloalkanes by types of structures is determined by the chemical composition of oil and the temperature limits of the fractions. Aromatic hydrocarbons - arenes with the empirical formula C₆H₆ are contained in oil, less than 10-15% by weight, and are represented by homologues of benzene and derivatives of polycyclic arenes. In hybrid hydrocarbon molecules, structural elements of all types exist: mono- and polycyclic arenes, mono- and polycyclic five- or six-ringed cyclanes and alkanes of a normal and branched structure. They can be divided into three types: 1) alkane-cycloane; 2) alkane-arene and 3) alkane-cycloane-arene. Hybrid hydrocarbons with mono- or bicyclic arenes with long alkyl chains can be part of paraffins and ceresins. The third type of hybrid hydrocarbons is most common among hydrocarbons of high-molecular part of oil [2].

Abroad, when determining the qualitative indicators of oil, density and distillation models of quality are applied. In the density model, the quality of oil and, consequently, its cost parameters are associated with the density and sulphur content. The distillation model of oil quality and its cost is associated with the potential of light oil fractions. The attempt to bring the quality of domestic oil to world standards led to the fact that in 1989 in our country for the first time in additions to GOST 9965 "Oil for oil refineries. Technical conditions" density and mass content of sulphur were proposed as the main indicators characterizing the consumer properties of oil [3]. Today, the following physicochemical properties of oil are indicated: the yield of fractions at temperatures up to 200, 300 and 350 degrees; oil density \( \rho \); mass fraction of sulphur \( S \); concentration of chloride salts. In TU 39-1623-93 "Russian oil supplied for export", according to the listed physicochemical properties, oil is divided into four types (Table 1).

### Table 1. Classification of oil supplied for export.

| Indicator | Norm for type |
|-----------|---------------|
| 1. Density at 20 °C, kg/m³, not more than | \( \leq 850 \) | \( \leq 870 \) | \( \leq 890 \) | \( \leq 895 \) |
| 2. Fraction output, volumetric %, not less than | | | | |
| at a temperature up to 200°C | \( \geq 25 \) | \( \geq 21 \) | \( \geq 21 \) | \( \geq 19 \) |
| at a temperature up to 300°C | \( \geq 45 \) | \( \geq 43 \) | \( \geq 41 \) | \( \geq 35 \) |
| at a temperature up to 350°C | \( \geq 55 \) | \( \geq 53 \) | \( \geq 50 \) | \( \geq 48 \) |
| 3. Mass fraction of sulphur, %, not more than | \( \leq 0.6 \) | \( \leq 1.8 \) | \( \leq 2.5 \) | \( \leq 3.5 \) |

### 2. Research

In the course of the study, the quality of oil in the following fields of Western Siberia was determined: Ust-Balykskoye, Ombinskoye, Vostochno-Surgutskoye, Yuzhno-Surgutskoye, Fainskoye. We experimentally determined the following quality indicators: fractional composition, density of oil, mass fraction of sulphur, concentration of chloride salts, kinematic viscosity, water content. Fractional composition is the defining characteristic when establishing the field of application of petroleum products. The limits guarantee the quality of products with the corresponding characteristics of volatility. The essence of the method is the distillation of 100 cm³ of the test sample in an automatic apparatus and the chromatographic determination of the indicators under conditions corresponding to the nature of the product and conducting constant observations of the thermometer readings and condensate volumes. The density of oil and oil products was determined by a pycnometer. The method is based on the determination of the relative density - the ratio of the mass of the test product to the mass of water taken in the same volume and at the same temperature. Since a mass of 1 cm³ of water is taken as a unit of mass at a temperature of 4 °C, the density expressed in g/cm³ will be numerically equal to the density with respect to water at a temperature of 4 °C. The essence of the method for determining the mass fraction of sulphur was that the test sample was placed in a beam of rays emitted
by an X-ray source. The characteristics of the excitation energy from the X-ray radiation were measured and the obtained signal of the pulse counter was compared with the counter signals obtained by testing the pre-prepared calibration samples. The main method for determining the concentration of chloride salts was the extraction of chloride salts from oil by water and indicator or potentiometric titration into aqueous extracts. Determination of the kinematic viscosity consisted in measuring the time elapsed (seconds) by a certain volume of the test fluid under the influence of gravity at a constant temperature by a calibrated glass viscometer. The essence of the method for determining the water content consists in heating a sample of oil with a water-insoluble solvent (for example, with Separol demulsifier) and measuring the volume of condensed water.

3. Results and discussion
The chemical experiment was carried out in several stages. The task of the first stage of the experiment was to test the fractional composition. The regulators of the device were set in the positions corresponding to the sample and the test conditions for this group. The device automatically records the initial boiling point, the end point and recorded the distillation curve in the evaporation temperature coordinates - the percentage of distillation. The device controlled the time interval between the start of the test and the initial boiling point, the set distillation rate and the final heating control. After cooling the flask, the cooled liquid remaining in the flask was poured into a graduated cylinder with a division value of 0.1 cm³ and volume was recorded. The volume was added to the percentage of distillation to obtain the total amount of distillation. An uncorrected percentage of losses was calculated. From each stated evaporation percentage, distillation losses were subtracted to calculate the appropriate percentage of distillation and the thermometer reading corresponding to this percentage of distillation was determined from the distillation curve (Table 2).

Table 2. Fractional composition.

| Field              | Fractional distillation of oil, volume of distillation (ml), at temperature (°C) |
|--------------------|-----------------------------------------------------------------------------------|
| init. boil. | 100 | 120 | 150 | 160 | 180 | 200 | 220 | 240 | 260 | 280 | 300 |
| Ust-Balykskoye    | 70  | 3.0 | 7.0 | 10.0| 12.0| 14.5| 17.5| 21.0| 24.0| 28.0| 31.5| 35.5|
| Ombinskoye        | 58  | 5.5 | 9.5 | 14.5| 16.0| 20.5| 23.0| 27.5| 30.5| 33.5| 38.0| 41.0|
| Vostochno-Surgutskoye | 50  | 7.5 | 12.0| 18.0| 20.5| 25.0| 29.0| 33.0| 37.0| 41.0| 46.0| 50.5|
| Yuzhno-Surgutskoye | 62  | 4.0 | 7.0 | 12.0| 13.0| 16.0| 19.0| 22.5| 26.0| 30.0| 33.5| 37.5|
| Fainskoye         | 52  | 6.0 | 9.5 | 15.0| 17.0| 21.0| 24.0| 28.5| 33.0| 37.0| 41.5| 45.0|

Analysis of the fractional composition showed that the oil of the Yuzhno-Surgutskoye, Ust-Balykskoye fields does not meet the requirements of TU 39-1623-93. Fractional distillation of oil from the remaining fields shows quality results. The second stage of the experiment included determination of density. A pycnometer was selected based on the properties of the test product. The latter was weighed with an error of not more than 0.0005 g, if the capacity of the pycnometer was more than 25 cm³, and with an error of not more than 0.0002, if the capacity of the pycnometer was less than 25 cm³. The pycnometer, with the "water number" set, was filled with the test product at a temperature of 20 °C. The pycnometer was closed with a stopper, immersed in a thermostat at a temperature of 20 °C and kept until the level of the test product changed (at least 30 minutes). The density was calculated by the formula:

\[ \rho_1 = \frac{(m_1 - m_0) \cdot \rho_c}{(m_c - m_0)} + C, \]

where \( \rho_1 \) - sample density at the determination temperature, kg/m³; \( \rho_c \) - water density at the sample oil temperature, kg/m³; \( m_0 \) - mass of the pycnometer in the air, g; \( m_c \) - mass of the pycnometer with water in the air at the sample oil temperature, g; \( m_1 \) - mass of the pycnometer with the sample in the air at the test temperature, g; \( C \) - correction for air pressure, kg/m³ (Table 3).
Table 3. Oil density.

| Field                  | Density of drained oil by pycnometer, kg/m³ |
|------------------------|--------------------------------------------|
| Ust-Balykskoye        | 876.6                                      |
| Yuzhno-Surgutskoye    | 866.2                                      |
| Ombinskoye            | 868.2                                      |
| Vostochno-Surgutskoye | 836.4                                      |
| Fainskoye             | 846.6                                      |

The density of drained oil by a pycnometer, kg/m³, showed the quality results of the Vostochno-Surgutskoye and Fainskoye fields.

The third stage of the experiment was connected with the determination of the sulphur concentration. 3/4 of the volume of the cuvette was filled with the test sample. Viscous samples were heated to ensure their fluidity; air bubbles were absent in the space between the cuvette window and the surface of the sample. Each sample was measured according to the recommended counting time for a certain concentration range. The sulphur concentration in the sample was calculated automatically from the calibration curve (Table 4).

Table 4. Mass fraction of sulphur.

| Field                  | Sulphur content of oil, % |
|------------------------|---------------------------|
| Ust-Balykskoye        | 1.75                      |
| Yuzhno-Surgutskoye    | 1.74                      |
| Ombinskoye            | 1.14                      |
| Vostochno-Surgutskoye | 1.16                      |
| Fainskoye             | 1.22                      |

The sulphur content of oil corresponds to the norms of TU 39-1623-93 for all fields.

The fourth stage of the experiment was connected with the determination of the concentration of chloride salts by their potentiometric titration in aqueous extract. The sample of the analysed oil was stirred for 10 minutes, shaking in a bottle filled 2/3 of its capacity, then the sample of the analysed oil was transferred to a separatory funnel with a stirrer. The remainder of oil was removed from the pipette walls with toluene. 100 cm³ of hot distilled water were added to the sample of the analysed oil and the chloride salts were extracted by stirring for 10 minutes. If an oil emulsion formed during the extraction of chloride salts, then a 2% demulsifier solution was added to destroy it. During potentiometric titration of aqueous extracts of chloride salts, it was evaporated to a volume of 15 cm³ in a 150-cm³ beaker, then transferred to a titration beaker. Then it was cooled to room temperature, 7 cm³ of acetone was added, acidified with 6 mol/dm³ sulfuric acid solution and titrated. The mass concentration of chloride salts (X1) in milligrams of sodium chloride per 1 dm³ of oil was calculated by the formula:

\[
X_1 = \frac{(V_1 - V_2) \cdot T \cdot 1000 \cdot A}{V_3},
\]

where \( V_1 \) - volume of 0.005 mol/dm³ of a solution of mercuric nitrate or 0.01 mol/dm³ of silver nitrate during potentiometric titration consumed for titration of aqueous extract, cm³; \( V_2 \) - volume of 0.005 mol/dm³ of a solution of mercuric nitrate or 0.01 mol/dm³ of silver nitrate during potentiometric titration consumed for titration of solution in the control experiment (without an oil sample), cm³; \( V_3 \) - volume of oil taken for analysis, cm³; \( T \) - titre of 0.005 mol/dm³ of a solution of mercuric nitrate or 0.01 mol/dm³ of silver nitrate during potentiometric titration, in milligrams of sodium chloride per 1 cm³ of solution; 1000 - coefficient for recalculating the mass concentration of chloride salts in 1 dm³ of oil; \( A \) - coefficient expressing the ratio of the volume to which the aqueous extract of the analysed oil was diluted to the volume of the solution taken from the volumetric flask for titration (when titrating the entire aqueous extract of the coefficient \( A = 1 \)). The mass fraction of chloride salts in oil in percentage of sodium chloride (X2) was calculated by the formula:
\[ X_2 = \frac{X_1 \cdot 100}{BC \rho}, \]

where \( X_1 \) - mass concentration of chloride salts in oil in milligrams of sodium chloride per 1 dm\(^3\) of oil; \( B \) and \( C \) - conversion factors for cubic decimetres into cubic centimetres (1000) and grams into milligrams (1000); \( \rho \) - density of the analysed oil, g/cm\(^3\).

**Table 5. Concentration of chloride salts.**

| Field                     | Chloride salts in emulsion, mg/dm\(^3\) |
|---------------------------|------------------------------------------|
| Ust-Balykskoye           | 114.2                                    |
| Ombinskoye               | 214.6                                    |
| Vostochno-Surgutskoye    | 21.7                                     |
| Yuzhno-Surgutskoye       | 31.8                                     |
| Fainskoye                | 14.5                                     |

The maximum content of salts was determined in the Ust-Balykskoye and Ombinskoye oil fields, which does not meet the requirements of TU 39-1623-93.

The fifth stage was based on the method of determining the water content. The test included heating the flask to boiling so that the rate of condensation of the distillate into the receiver was 2 to 5 drops per second. The distillation was stopped as soon as the volume of water in the receiver-trap took the temperature of the air in the room. The volume of water was recorded, with an accuracy up to one upper division of the part of the receiver-trap occupied with water. The mass (\( X \)) or volume (\( X_1 \)) fraction of water was calculated by the formulas:

\[ X = \frac{V_0}{m} \cdot 100, \quad X_1 = \frac{V_0}{V} \cdot 100, \]

where \( V_0 \) – volume of water in the receiver, cm\(^3\); \( m \) – sample mass, g; \( V \) – sample volume, cm\(^3\) (Table 6).

**Table 6. Water content.**

| Field                     | Water content in oil, % vol. |
|---------------------------|-------------------------------|
| Ust-Balykskoye            | 0.70                          |
| Yuzhno-Surgutskoye        | 0.20                          |
| Ombinskoye                | 0.50                          |
| Vostochno-Surgutskoye     | 0.10                          |
| Fainskoye                 | 0.01                          |

The water content was discovered in abundance at the Ust-Balykskoye field.

At the stage of determining the kinematic viscosity, the selected oil sample was heated in a container for 1 hour (at 60 °C). The sample was stirred and shaken. After the flowability was reached, the sample was poured into a glass flask with a capacity of 100 cm\(^3\) in the amount to fill the two viscometers. It was heated for 30 minutes in a bath with boiling water. Two viscometers were filled. If the sample was heat treated before the test, a pre-heated filter was used to prevent coagulation. The time was measured to within 0.1 s. This time was required for the sample to pass from the first mark of the viscometer to the second [4]. The kinematic viscosity \( v \), mm\(^2\)/s, was calculated by the formula:

\[ v = C \cdot t, \]

where \( C \) — calibration constant of viscometer, mm\(^2\)/sec; \( t \) — arithmetic mean value of the flow time, sec. The dynamic viscosity \( \eta \), MPa·s, was calculated from the kinematic viscosity:

\[ \eta = v \cdot \rho \cdot 10^{-3}, \]

where \( \rho \) — density at the same temperature at which the kinematic viscosity was determined, kg/m\(^3\); \( v \) — kinematic viscosity, mm\(^2\)/s. The results of the tests are given in Table 7.
Table 7. Kinematic viscosity.

| Field                | Kinematic viscosity of oil, mm²/sec |
|----------------------|-------------------------------------|
|                      | 20 °C  | 50 °C  |
| Ust-Balykskoye       | 30.61  | 10.19  |
| Yuzhno-Surgutskoye   | 17.80  | 7.09   |
| Ombinskoye           | 18.03  | 7.05   |
| Vostochno-Surgutskoye| 5.51   | 2.86   |
| Fainskoye            | 8.02   | 3.81   |

The kinematic viscosity of oil from the Vostochno-Surgutskoye and Fainskoye fields corresponds to the norms of TU 39-1623-93.

4. Conclusion
On the basis of the results of the oil studies, the following conclusion can be drawn: from all the fields studied, oil from Vostochno-Surgutskoye and Fainskoye meets all the requirements of TU 39-1623-93 for export raw materials, while most of the investigated oil does not meet these standards for a number of parameters. A comparative analysis of the quality of oil by its physico-chemical characteristics underlies the development and implementation of the development strategy of Russia in the field of fuel and energy complex.

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