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Phisical and chemical properties and thermobaric conditions of occurrence of hard-to-recover oils

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Abstract

The criteria necessary to classify oils as hard-to-recover oil reserves are determined. The distribution of viscosity, heavy, paraffin and highly resin oils is analyzed in terms of their reserves. The features of the physic-chemical properties of these oils are studied under various conditions of their occurrence and formation temperatures. The results obtained could be used to solve practical issues in the oil sector. *Copyright* © 2014 International Energy and Environment Foundation - All rights reserved.

Keywords: Hard-to-recover oils; High-viscosity oils; Heavy oils; Paraffin oils; Highly resin oils; Physical and chemical properties of oils; Conditions of occurrence; Formation temperature; Reservoir pressure; Gas content in oil.

1. Introduction

Regularities of spatial distribution and characteristics of physical and chemical properties of oils were considered in [1-4]. Currently, the world has witnessed the growth of the share of hard-to-recover oils in the total balance due to the depletion of readily available oils. The oils in complex geological formations and deposits or those containing low-mobility oils (e.g., high-viscosity, high-paraffin oils) are classified as hard-to-recover reserves. They are characterized by relatively low flow rates due to low reservoir productivities, unfavorable conditions of oil occurrence (gas and oil deposits at the depths more than 4,500 meters, etc.) or anomalous physical and chemical properties. Currently, however, systematic materials on the properties of such oils in the literature is extremely insufficient. In this regard, the aim of our work was the consideration of physical and chemical properties of hard-to-recover oils and features of the conditions of their occurrence.

2. About hard-to-recover oils

The most reasonable approach to the differentiation of hard-to-recover reserves was proposed by Khalimov in 1987. Purtova and coauthors of [5] made a list of the main criteria for differentiation of hard-to-recover reserves, according to which the such oil reserves are characterized by their specific properties and conditions of their occurrence, namely:

- (1) oil reserves possessing anomalous physical and chemical properties (high viscosity and density and high content of paraffins, asphaltenes and resins);
- (2) oil reserves in low permeability reservoirs and oil-water and oil-gas zones;
- (3) oil reserves with high gas saturation (more than 200m³/m) or with dissolved and/or free gas containing aggressive components (hydrogen sulfide, carbon dioxide) in the amounts requiring the use of special equipment for well-drilling and oil production;

- (4) oil reserves occurring at great depths (below 4,500m);
- (5) oil reserves with the reservoir temperature of 100°C and higher or less than 20°C (due to the little difference between the low reservoir temperature and the pour point of wax and resins);
- (6) oil reserves with a high degree of water cut (to 75 80%).

Recent years have seen an incressed production of hard-to-recover oils with anomalous physical and chemical properties, i.e. paraffin, resin, viscosity and heavy oils. An investigation of these oils requires the development of the respective EOR methods, which in turn makes it necessary to identify patterns of their spatial distribution and to analyze the changes in their physico-chemical properties that depend on the geological and thermobaric conditions of their occurrence. The development of new technologies for production and transportation of oils with anomalous physical and chemical properties and improvement of the available processes require that new data on the properties and conditions of occurrence of hard-to-recover oils be obtained.

The reserves of heavy and viscosity oils are several times higher than those of readily available lowviscosity oils (810 and 162 billion tons, respectively) and represent a raw material source for the oil sector of Russia and other oil-producing countries of the world [6-10]. The development of deposits of viscosity oils is therefore receiving an increasing attention. To date, the average annual total production of these oils in the world is approaching 500 million tons and the cumulative production exceeds 14 billion tons. The most abundant resources of heavy and viscous oil are located in Canada and Venezuela. Mexico, the United States, Russia, Kuwait; China also possess significant heavy oil reserves. On the territory of Russia, the reserves of oil with a viscosity higher than 35 mm²/s account for 7.3 billion tons oil and most of them are concentrated in the Komi Republic, Tatarstan, and in the Tyumen region. Paraffin crude oils [11, 12], whose viscosity and high pour point are controlled by the high paraffin content (more than 6%) make a considerable fraction in the total reserves of viscous oils. The percentage of paraffin oils is also significant and accounts for more than 25% of all world oils. In particular, 19% of oil fields on the territory of the West Siberian oil-gas basin contain paraffinic oils.

The investigations requiring an analysis of numerous literature sources need the data on physical properties and chemical composition of the global oils and on the geological characteristics of oil bearing basins. A large body of information has been accumulated in the data base on physical and chemical oil properties [13] of the Institute of Petroleum Chemistry, SB RAS (Tomsk). Therefore this data base was used as a source of information on hard-to-recover oils.

The data base includes more than 22,000 oil samples from 191 oil and gas basins of the world, most are those of Eurasian continental oils from 106 oil and gas basins and 4,064 oil fields located in 58 countries. The general characteristics of the data base are presented in Table 1. Being constantly developed and improved, the database is enriched with new data on the physical, chemical and geochemical properties of oils, their geographical location, geological modes of occurrence and formation temperature and pressure. Table 1 offers a description of the continental distribution of the database information.

| Geography | Data base sample | Number of oil-gas bearing basins | Number of oil fields |
|------------------------------------|------------------|----------------------------------|----------------------|
| Australia, New Zealand and Oceania | 152 | 11 | 86 |
| Africa | 532 | 15 | 294 |
| Eurasia | 20,629 | 106 | 4,064 |
| North and Central America | 1,631 | 38 | 899 |
| South America | 428 | 21 | 256 |

Table 1. Data distribution by continents

The global database on physical and chemical properties of oils currently contains 5,104 heavy oil samples, 2,510 samples of viscous oil (with a viscosity higher than 35mm²/s), 2,327 paraffin oil, and more than 2,000 resin oil samples (more than 13 % resin). More detailed characteristics of this information are presented in Table 2.

3. Generalized classification of oils by their physical and chemical parameters

To investigate the physical and chemical properties of hard-to-recover types of oils having anomalous physical and chemical properties and those with properties conditioned by anomalous modes of occurrence, we have developed a generalized classification of oils (Tables 3 and 4).

| Class of oil | Data base sample | Number of oil-gas bearing basins | Number of oil fields |
|--|------------------|----------------------------------|----------------------|
| Heavy (density $> 0.88 \text{ g/cm}^3$) | 5,104 | 117 | 1,637 |
| Viscous (viscosity at 20 °C > 35 mm ² /s) | 2,510 | 63 | 821 |
| Resin (resin content >13 %) | 2,030 | 52 | 684 |
| Paraffin (paraffin content > 6 %) | 2,327 | 58 | 800 |

Table 2. Characteristics of database information on the oils with anomalous properties

Table 3. Classification of oils by their density and viscosity

| Index | Class of | oil | Limits of variation |
|------------------------------------|-----------|------------------------------|---------------------|
| Density | very ligh | t oil | < 0.80 |
| (g/cm^3) | light oil | | 0.80÷0.84 |
| | medium- | density oil | 0.84÷0.88 |
| | heavy | higher-density oil | 0.88÷0.92 |
| | | extra heavy crude oil | 0.92÷0.96 |
| | | bituminous oil | > 0.96 |
| Viscosity at 20 | low-visco | osity oil | < 10 |
| $^{\circ}C$, (mm ² /s) | medium- | viscosity oil | 10 ÷35 |
| | viscous | higher-viscosity oil | 35÷100 |
| | | high-viscosity oil | 100÷500 |
| | | extremely-high-viscosity oil | > 500 |

| Chemical component, wt% | Class of oil | | Limits of variation |
|------------------------------|-------------------------------|------------------------|---------------------|
| Sulfur content, wt% | low sulphur (sweet crude) oil | | < 0.5 |
| , | medium sulphur oil | | 0.5÷1 |
| | sulfurous oil | | 1÷3 |
| | high-sulphur (s | sour) oil | > 3 |
| Resin content, wt% | low-resin oil | | < 8 |
| , | medium-resin | oil | 8÷13 |
| | resin oil | moderately resin | 13÷20 |
| | | highly resin | 20÷30 |
| | extremely resin | | > 30 |
| Asphaltene content, wt% | low-asphaltene | • | < 3 |
| - | medium-aspha | | 3 ÷10 |
| | high-asphalten | e oil | > 10 |
| Paraffin content, wt% | low-paraffin oil | | < 1.5 |
| | medium-paraf | fin oil | 1.5÷6 |
| | paraffin oils | moderately paraffin | 6÷10 |
| | | highly paraffin | 10÷20 |
| | | extremely paraffin | > 20 |
| Low-boiling fraction 200 °C, | oils with low f | raction-200 | < 20 |
| wt% | oils with medi | um fraction-200 | $20 \div 30$ |
| | oils with high fraction-200 | | > 30 |
| Low-boiling fraction 350 °C, | oils with low fraction-200 | | < 25 |
| wt% | oils with medi | um fraction-350 | 25÷50 |
| | oils with high | fraction-350 | 50÷75 |
| | oils with extrem | mely high fraction-350 | 75÷100 |

4. Analysis of oil distribution by classes

Figure 1 shows the diagrams of distribution of oil types under study by classes in terms of their density, viscosity and content of resins and paraffin. As can be seen from Figures 1a and b, the amount of oil types (light, medium, and heavy oils and low-viscosity, medium-viscosity, and viscous oils) are almost equally distributed by classes, i.e. light, medium density, low viscosity and medium viscosity oils comprise more than 66% of the total sampling. Heavy and viscous oil account for slightly more than 33% of the total sample, and resinous and paraffin oils account for less than 30% in the total sample (Figures 1c and d).

Here we investigate the distribution of hard-to-recover oil reserves (heavy, viscosity, paraffin, and resin) in the Volga-Ural, West Siberian, and Timan-Pechora oil and gas bearing basins (in what follows referred to as Volga-Ural, West Siberian, and Timan-Pechora oil-gas-bearing basins, respectively) as the main Russian oil producing regions. Table 5 shows the distribution of information from the data base for these three basins. These data indicate that the most abundant reserves of viscous, heavy, paraffin, and resin oils are located in Western Siberia; the Volga-Ural basin possesses rich reserves of viscosity, heavy, and resin oils, while the Timan-Pechora basin has concentrated reserves of paraffin oils. The largest number of fields with hard-to-recover oils is located in the Volga-Ural oil-producing regions and the lowest – in the Timan-Pechora basin.



Figure 1. The distribution of the number of deposits by density (a), viscosity (b), content of resin (c) and paraffin (d)

5. Features of the physic-chemical properties of hard-to-recover oils

As already mentioned above, the hard-to-recover oils also include those with a gas factor above $200 \text{ m}^3/\text{t}$. The database contains 348 samples of these oils from 255 oil fields of 44 basins. They are distributed over the continents as follows: one – in Australia, 3 – in Africa, 20 – in America and the rest 20 – in Eurasia. Most deposits with high gas content are located in the Volga-Ural (81 deposits), 10 deposits – in the Lena-Tunguss, and 7 deposits each in Western Canadian, Pre-Caspian and Timan-Pechora basins. The physic-chemical properties of these oils are presented in Table 6. It is evident that, according to

Tables 3 and 4, these oils belong to the light, low viscosity, low sulfur, moderately paraffin, and low asphaltene oils.

| Statistical data | Oil-gas bearing basins | | | | |
|-------------------------|------------------------|---------------|---------------|--|--|
| | Volga-Ural | West Siberian | Timan-Pechora | | |
| | Viscous o | oils | | | |
| Number of samples | 1,263 | 157 | 104 | | |
| Number of oil fields | 362 | 45 | 42 | | |
| Russian oil reserves, % | 33.46 | 37.06 | 14.30 | | |
| | Heavy oils | | | | |
| Number of samples | 1,787 | 378 | 270 | | |
| Number of oil fields | 453 | 120 | 60 | | |
| Russian oil reserves, % | 38.35 | 40.70 | 9.85 | | |
| | Paraffin o | oils | | | |
| Number of samples | 322 | 449 | 95 | | |
| Number of oil fields | 140 | 136 | 34 | | |
| Russian oil reserves, % | 16.26 | 40.46 | 42.50 | | |
| Resin oils | | | | | |
| Number of samples | 1,103 | 133 | 66 | | |
| Number of oil fields | 301 | 58 | 24 | | |
| Russian oil reserves, % | 45.87 | 36.46 | 9.79 | | |

Table 5. Hard-to-recover oils in the main oil-gas bearing basins of Russia

Table 6. Physical and chemical properties of crude oils with high gas content (above $200m^3/t$)

| Physic-chemical parameters | Database sample | Mean value | |
|--|-----------------|------------|--|
| Density g/cm ³ | 326 | 0.83 | |
| Viscosity at 20 °C, mm ² /s | 148 | 7.21 | |
| Sulfur content, wt% | 248 | 0.38 | |
| Paraffin content, wt%. | 173 | 6.23 | |
| Resin content, wt% | 104 | 5.30 | |
| Asphaltene content, wt% | 126 | 0.82 | |
| Low-boiling fraction 200 °C, wt% | 23 | 31.60 | |
| Low-boiling fraction 300 °C, wt% | 23 | 48.28 | |
| Gas content in oil, m^3/t | 348 | 346.19 | |
| Thermobaric conditions of occurrence | | | |
| Reservoir temperature, °C | 241 | 85.88 | |
| Reservoir pressure, MPa | 232 | 32.54 | |

The presence of sulfur dioxide also impedes oil production due to the increased environmental hazard, which requires the use of special equipment for well drilling and oil production when the concentration of sulfur dioxide in the oil is higher than 5%. The database comprises 79 samples of oils containing sulfur dioxide gas from 55 oil fields of 19 basins. The physical and chemical properties of these oils are presented in Table 7. It is evident from Table 8 that the oils belong to medium density, high viscosity, sulfurous, medium paraffin, medium asphaltene and moderately resin classes.

The main criteria for differentiation of hard-to-recover reserves are the oil reservoir temperatures above 100°C or below 20°C. The database contains 838 samples of in-reservoir oils at the temperatures higher 100°C from 483 oil fields of 47 basins. Their physic-chemical properties are presented in Table 8. It implies that these oils belong to the light, medium viscosity, low sulfur, low resin and low asphaltene but moderately paraffin classes.

The data base contains 318 samples of oils occurring in low-temperature reservoirs (< 20 °C) from 181 deposits of 35 basins. The most of oil deposits characterized by low reservoir temperature are located in the Volga-Ural basin (81 deposits), the Lena-Tunguss basin (10 deposits) and in Western Canadian, Pre-Caspian and Timan-Pechora basins (7 deposits each). Their physical and chemical properties are

presented in Table 9. It is evident from Table 9 that these oils belong to the high-density, extremely high-viscosity, sulfur, medium paraffin, moderately resin, medium asphaltene and low gas content oil classes.

| Physic-chemical parameters | Database sample | Mean value | |
|--|-----------------|------------|--|
| Density, g/cm ³ | 23 | 0.8767 | |
| Viscosity at 20 °C, mm ² /s | 10 | 49.33 | |
| Sulfur content, wt% | 19 | 2.18 | |
| Paraffin content, wt% | 13 | 4.05 | |
| Resin content, wt% | 12 | 14.56 | |
| Asphaltene content, wt% | 11 | 6.23 | |
| Gas content in oil, m^3/t | 15 | 109.97 | |
| Thermobaric conditions of occurrence | | | |
| Reservoir temperature, °C | 27 | 74.75 | |
| Reservoir pressure, MPa | 30 | 31.81 | |

Table 7. Physic-chemical properties of crude oils with high sulfur gas content (above 5%)

Table 8. Physical and chemical properties of in-reservoir oils at the temperature above 100°C

| Physic-chemical parameters | Database sample | Mean value | |
|--|-----------------|------------|--|
| Density, g/cm ³ | 432 | 0.8251 | |
| Viscosity at 20 °C, mm ² /s | 155 | 12.03 | |
| Sulfur content, wt% | 237 | 0.36 | |
| Paraffin content, wt% | 228 | 9.85 | |
| Resin content, wt% | 214 | 5.36 | |
| Asphaltene content, wt% | 203 | 1.27 | |
| Low-boiling fraction 200 °C, wt%. | 75 | 29.41 | |
| Low-boiling fraction 300 °C, wt%. | 64 | 49.10 | |
| Gas content in oil, m^3/t | 117 | 163.63 | |
| Thermobaric conditions of occurrence | | | |
| Reservoir temperature, °C | 838 | 119.40 | |
| Reservoir pressure, MPa | 665 | 38.31 | |

Table 9. Physical and chemical properties of in-reservoir oils at the temperature lower than 20 °C

| Physic-chemical parameters | Database sample | Mean value | |
|--|-----------------|------------|--|
| Density, g/cm ³ | 221 | 0.8855 | |
| Viscosity at 20 °C, mm ² /s | 165 | 12,929.34 | |
| Sulfur content, wt% | 137 | 1.46 | |
| Paraffin content, wt% | 126 | 3.87 | |
| Resin content, wt% | 112 | 14.52 | |
| Asphaltene content, wt% | 106 | 3.98 | |
| Low-boiling fraction 200 °C, wt%. | 24 | 18.75 | |
| Low-boiling fraction 300 °C, wt%. | 24 | 33.13 | |
| Gas content in oil, m ³ /t | 104 | 36.82 | |
| Thermobaric conditions of occurrence | | | |
| Reservoir temperature, °C | 318 | 15.37 | |
| Reservoir pressure, MPa | 267 | 10.04 | |

A comparison of the data from Tables 8 and 9 has shown that oil properties are strongly controlled by the formation temperature. The highest quality indicators are exhibited by the oils occurring in high-temperature reservoirs.

Deep-seated oils (below 4,500m) are also hard-to-recover reserves. There are 354 samples from 180 deposits of 24 basins in the data base. An analysis of their physical and chemical properties presented in Table 10 has revealed that in general they can be classified as light, high-viscosity, medium-sulphur,

medium-paraffin, low-resin, low-asphaltene oils with a high content of low-boiling (200°C) fraction and average content of low-boiling (300°C) fraction. These oils are characterized by a high content of oil gas, which is also complicates oil production.

Table 10. Physical and chemical properties of oils from deep-lying strata (more than 4,500m)

| Physic-chemical parameters | Database sample | Mean value | |
|--|-----------------|------------|--|
| Density, g/cm ³ | 153 | 0.8377 | |
| Viscosity at 20 °C, mm ² /s | 72 | 79.15 | |
| Sulfur content, wt% | 104 | 0.52 | |
| Paraffin content, wt% | 66 | 5.92 | |
| Resin content, wt% | 59 | 5.91 | |
| Asphaltene content, wt% | 62 | 1.81 | |
| Low-boiling fraction 200 °C, wt%. | 47 | 32.14 | |
| Low-boiling fraction 300 °C, wt%. | 32 | 46.57 | |
| Gas content in oil, m ³ /t | 9 | 263.24 | |
| Thermobaric conditions of occurrence | | | |
| Reservoir temperature, °C | 77 | 117.48 | |
| Reservoir pressure, MPa | 77 | 66.73 | |

6. Conclusion

Currently, production of hard-to recover reserves increases due to depletion of readily available oils in the whole world. Here we have identified the criteria for classification of oils as hard-to-recover reserves. Using a global database on physical and chemical properties of oils, we have analyzed the distribution of viscous, heavy, paraffin and highly resin oils in terms of the volume of their reserves. In order to specify the physical and chemical properties of these oils as a function of the conditions and the depth of their occurrence and the reservoir-temperature differences, a generalized classification of oils by their density, viscosity and chemical composition has been developed. The results obtained can be used to develop new methods of enhanced oil recovery, to improve the available technologies, to optimize the transportation of oils with anomalous physical and chemical properties, and to solve a number of related oil-sector problems.

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