

# Estimation of Potential Capability of Natural Bitumens and High Viscosity Oils for Refining According to Fuel-Bitumen Scheme

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## Abstract

According to different estimates, geological heavy oil and natural bitumens resources at the Tatarstan deposits make 1,5-7 billion tons. On the territory of Tatarstan across all bituminous horizons about 450 deposits of natural bitumens have been found. One third of deposits of this raw materials existing in Russia fall on the share of Tatarstan. Natural bitumens are valuable material for production of fine chemicals that are used in different spheres of life activities. Natural bitumen is to a different extent oxidized high-viscosity oils of liquid, semi-liquid and hard texture with high content of sulfur, resins and asphaltenes. In contrast to oil, they are characterized by increased content of vanadium, nickel, molybdenum and significantly smaller content of gasoline and diesel fractions. Nevertheless, despite the works performed, no significant success has been achieved in production and processing of bitumens yet. This is mainly because of absence of the relevant equipment. It is necessary to accelerate development of bituminous deposits, creation of complexes with the use of high performance technologies and technical means for most complete extraction of this raw material from the earth and treatment thereof. Implementation thereof will create pre-requisites for commercial exploitation of natural bitumens deposits not only in Tatarstan but in other regions of the Russian Federation as well. To estimate the potential capability of natural bitumens and high viscosity oils it is necessary to perform detailed analysis aimed at determining the graphical charts of the true temperature curve, density, low-temperature, viscosity properties, fraction and hydrocarbon composition.

**Keywords:** Bitumens, Bituminous Materials, Fuels, Additives, High Viscosity Oils, Natural Bitumens, Processing, Refining, True Temperature Distillation Curve

## 1. Introduction

At the current stage the strategic trend of development of the oil and gas industry is increase in the oil conversation depth with the use of relatively new approaches and methods of mining, treatment, transporting and processing of different kinds of Hydrocarbons (HC)<sup>1,2</sup>.

## 2. Materials and Methods

The provided sample of natural bitumen from the Nagornoye deposit contained 30% of water. After

dehydration the sample was subjected to analysis aimed at integral determination of the main physico-chemical properties and component composition<sup>1</sup>. The results of analysis of the natural bitumen from the Nagornoye deposit are presented in the Table 1.

As it follows from the Table 1, by content of asphalt-resinous matters (39,8% wt.) the natural bitumen under investigation is referred to the 'maltha' class (35-60% wt.). Upon high content of resinous-asphalt-new substances natural bitumen features small paraffin content (0,5% wt.). High sulfur content is also peculiar to this natural bitumen (3,4% wt.).

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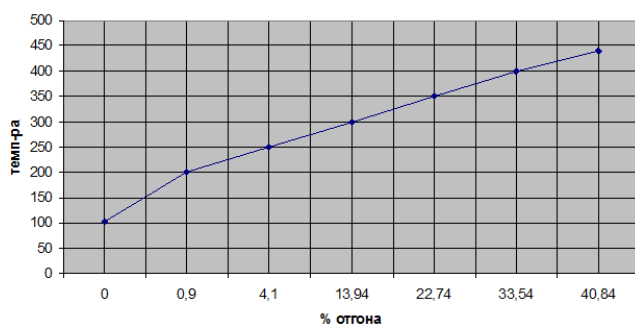
**Table 1.** Indicators of the natural bitumen of the Nagornoye deposit

| Indicators                   | Values |
|------------------------------|--------|
| Relative density, $p_4^{20}$ | 1,02   |
| Content, % wt.               |        |
| Sulfur                       | 3,4    |
| Asphaltenes                  | 21,8   |
| Silica gel resins            | 18,0   |
| Paraffin                     | 0,5    |
| Carben carboides             |        |
| Mechanical impurities        | -      |
| Bubble point, °C             | 106    |
| Fraction content, % wt.      |        |
| HK-200°C                     | 0,9    |
| 200-250°C                    | 3,2    |
| 250-300°C                    | 9,84   |
| 300-350°C                    | 8,8    |
| 350-400°C                    | 10,8   |
| 400-440°C                    | 7,3    |
| Above 440°C                  | 59,16  |

Figures of stripping to specified temperatures are presented in the Table 2; according to the data obtained the TTC of stripping to specified temperatures was designed and shown in Figure 1.

**Table 2.** Values of stripping to specified temperatures

| Oil fraction boiling range, °C | Stripping % |
|--------------------------------|-------------|
| 200                            | 0,9         |
| 250                            | 4,1         |
| 300                            | 13,94       |
| 350                            | 22,74       |
| 400                            | 33,54       |
| 440                            | 40,84       |
| above 440°C                    | 59,16       |


**Figure 1.** TTC of the natural bitumen from the Nagornoye deposit.

### 3. Results

As it follows from the above-specified results, the natural bitumen sample is characterized by insignificant distillate of gasoline and diesel fractions: 0,9 and 21,84% wt., respectively. The total yield of fractions distilled at above 300°C for natural bitumen makes 81,06 % wt. whereas for Devonian oil - 30-35% on the average and for carbonic oil - 39-42% wt. Such high yield of these fractions from the natural bitumen is achieved primarily due to the fractions distilled at above 400°C (66,46% wt.). These fractions are the main raw material for catalytic cracking plant and, therefore, by processing natural bitumen with the use of this plant much more of this fraction may be refined and is shown in Table 3. If we consider natural bitumen as raw material for production of bituminous pavements, then according to the classification presented in the Table 3 it is referred to the group of 'most suitable' for this purpose ( $A=21,8; R=18; P=0,5; 21,8+18-2,5*0,5=38,55$ , i.e.  $>8$ ).

**Table 3.** Classification of oils by their fitness for production of bituminous

| Group | Dependence between content of asphaltenes, resins and paraffin in oil (in % wt.) | Oil fitness for production of bituminous pavements |
|-------|--|--|
| I     | $A + R - 2,5 P > 8$  | Most fit   |
| II    | $A + R - 2,5 P$ from 0 to 8<br>At $A + R > 6$                                    | Fit  |
| III   | $A + R - 2,5 P < 0$ as well as<br>$A + R - 2,5 P > 0$ ,<br>But at $A + R < 6$    | Unfit  |

The use of natural bitumens for production of bituminous pavements and different bituminous products proves that recovery thereof may be economically viable since extraction, transportation and processing of natural bitumens according to the traditional procedure makes them non-competitive as compared to 'ordinary' oils<sup>2-5</sup>.

Since gasoline fraction is present in a slight amount (0,9% wt.) the analysis was started from the diesel fraction.

Two fractions were tested for pour point:

Sample No. 1: diesel fraction with distillate temperature up to 300°C.

Sample No. 2: diesel fraction with distillate temperature up to 350°C.

The provided samples correspond to the summer diesel fuels type by the pour-point temperature. As could be expected, with increase in the distillation degree the pour-point temperature increases: for the sample no. 1 –

pour-point temperature (tpour-point) makes minus 24°C; for the sample 2 – tpour-point. = minus 19°C.

In order to reduce the pour-point temperature in the sample No. 2 (with higher pour-point) synthetic depressor additive<sup>6,7</sup> was introduced in the amount 0,1% wt. the pour-point decreased to 35°C, i.e. the depressor effect made 16°C.

Thus, with the use of depressor additive<sup>8</sup> the summer diesel fuel was adjusted to the requirements to winter fuel is shown in Table 4.

Indicators of the diesel fraction distilled to 350°C modified through a depressor additive are presented in Table 4.

**Table 4.** Physico-chemical characteristics of modified diesel fraction distilled up to 350oC

| Indicators   | For our product | GOST 305 for winter fuel | Test methods |
|--|-----------------|--------------------------|--------------|
| Fraction composition is distilled over at the t, °C: |                 |                          |              |
| 50%  | 310             | not >250                 | GOST 2177-66 |
| 96%  | 350             | not >340                 |              |
| Kinematic viscosity at 20°C, cSt                     | 4,9             | 1,8- 5,0                 | GOST 33-82   |
| Density at 20°C, kg/m <sup>3</sup>                   | 826             | not >840                 | GOST 3900-85 |
| Copper plate test                                    | Withstands      | Withstands               |              |
| Flash point (closed cup), °C                         |                 | not < 35                 |              |
| Cloud point, °C                                      | -25             | not > (-25)              |              |
| Pour-point temperature, °C                           | -35             | not > (-35)              |              |
| Total sulfur content, % wt.                          |                 | not >0,5                 |              |

As it follows from the Table 4, modified diesel fuel distilled up to 350°C meets the requirements of the standard for winter diesel fuel. Introduction of additive in the diesel fuel distilled to 300°C results in further decrease in the pour-point temperature: from minus 24°C to minus 43°C.

Vacuum distilled fractions (>350°C; >400°C and > 440°C) were tested for compliance with the properties imposed on bitumens. Their characteristics are presented

in the Table 5. As follows from the comparison of the Table 5 and Table 6, fraction, etc. Thereafter the studies consisting in modifying the properties of gasoil cuts, namely production of bitumen-polymer compositions were performed.

**Table 5.** Fraction characteristics: >350°C, >400°C and > 440°C.

| Physico-chemical characteristics             | Oil fraction boiling range, °C |        |        |
|--|--------------------------------|--------|--------|
|  | >350°C                         | >400°C | >440°C |
| Ring-and-ball softening point, °C            | 40                             | 50     | 58     |
| Stretching property, cm                      | 44                             | 18     | 8,5    |
| Depth of needle penetration, 0,1 mm, at 25°C | 66                             | 20     | 10     |

The fraction > 350°C features the best indicators in terms of production of a bitumen-polymer composition. The impact of polymer bitumen component directly depends on oil fraction content in the latter. In this light it makes sense to use bitumens with lower softening point for mastic production. Besides, with increase in the softening point bitumen becomes hard and fragile as the asphaltenes content increases and the disperse medium become less elastic and frost-resistant. Addition of oil fractions results in improvement of low-temperature properties of the compound.

In order to estimate the possibility of use of heavy oil residue for production of bitumen-polymer compound this fraction > 350° C was modified using the sample of Low-molecular Polyolefin (LPO) - wax-like, semitransparent, hydrophobic substance of white color featuring high adhesion to different materials. The product consists of the mixture of saturated hydrocarbons primarily normal ones. The properties are presented in the Table 6.

**Table 6.** Physico-chemical characteristics of low-molecular polyolefin NPO

| Physico-chemical characteristics     | Values |
|--------------------------------------|--------|
| Melting point, °C                    | 90     |
| Dropping point, °C                   | 80     |
| Flash-point (open cup), °C           | 263    |
| Molecular weight                     | 1500   |
| Initial boiling point, °C:           | 330    |
| 5% boils off at the temperature, °C: | 405    |

Main performance characteristics of the bituminous composition obtained:

- Ring-and-ball softening point - 66 °C;
- Stretching property - 29 cm;
- Depth of needle penetration at 25°C - 95 mm ×0,1.

**Table 7.** Properties of cements MBR (bituminous-rubber cement) according to GOST 15836

| Physico-chemical characteristics                   | Mastic grade |        |        |         |
|--|--------------|--------|--------|---------|
|  | MBR-65       | MBR-75 | MBR-90 | MBR-100 |
| Ring- and-ball softening point, °C                 | 65           | 75     | 90     | 100     |
| Depth of needle penetration at 25°C, mm×0,1, not < | 40           | 30     | 20     | 1,5     |
| Stretching property, cm, not <                     | 4            | 4      | 3      | 2       |
| Water saturation during 24 hours, %, not >         | 0,2          | 0,2    | 0,2    | 0,2     |

Comparative analysis of properties of produced bituminous compound with the GOST 15836 requirements for insulating rubber mastics are shown in Table 7 as well as with properties of asphalt, construction and roofing bitumens<sup>8-11</sup> demonstrates that produced bituminous-polymer compound meets the requirements for mastic of the MBR-65.

The next stage of work was performance of studies aimed at reduction of viscosity of natural bitumen. Taking into account literature data about the positive effect of different kinds of exposure (ultrasonic, rotary-pulsed and other) on viscosity properties, natural bitumen was subjected to ultrasonic exposure at the plant UZDN-2T generating ultrasound with the frequency 22 kHz and processing on a Rotary-Pulsed-Acoustic Device (RPAD)<sup>12,13</sup>.

It was suggested that under influence of such processing change of the disperse structure of natural bitumen will take place and, as the result, reduction of its viscosity. The results of these studies are summarized in the Table 8.

**Table 8.** Impact of oil refining conditions on its viscosity.

| Oil under investigation   | Relative viscosity at 40°C, °VU |
|---|---------------------------------|
| Untreated oil   | 12,74                           |
| Oil after treatment with ultrasonic disperser UZDN for 10 minutes | 11,74                           |
| Oil after treatment with RPAD during 8 minutes at 7000 rpm        | 11,15                           |
| Oil after treatment with RPAD during 10 minutes at 10000 rpm      | 10,93                           |

As it follows from the Table 8 the optimal mode is oil treatment in the RPAD within 10 minutes with the rate 10,000 rpm. The oil viscosity is reduced from 12,74°VU to 10,93°VU, i.e. by 14,2%. The next stage was performance of studies aimed at increasing the yield of light oil fractions as the result of oil treatment with the use of the RPAD. It was suggested that under influence of such processing change of the disperse structure of natural bitumen will take place and, as the result, reduction of its viscosity. The results of these studies are summarized in the Table 9 and Table 10.

**Table 9.** Estimation of light fractions prior to RPAD processing viscosity.

| Oil fraction boiling range, °C | % wt. |
|--------------------------------|-------|
| 106-200                        | 1,8   |
| 200-250                        | 3,25  |
| 250-300                        | 71,55 |
| Σ                              | 76,6  |

**Table 10.** Estimation of light fractions after RPAD processing

| Oil fraction boiling range, °C | % wt. |
|--------------------------------|-------|
| 106-200                        | 2,1   |
| 200-250                        | 3,4   |
| 250-300                        | 72,6  |
| Σ                              | 78,1  |

The tests of the fraction 250-300°C at the pour point temperature were performed. The pour-point of the 250-300°C fraction makes minus 4°C. In order to reduce the pour-point temperature in the 250-300°C fraction synthetic depressor additives was introduced in the amount 0,1% wt. The pour-point decreased to 18°C, i.e. the depressor effect made 14°C.

## 4. Conclusions

As the result of the study it was established that treatment in a RPAD within 10 minutes at the rotation rate 10000 rpm provides increase in the light fraction yield by 1,5%. It was found that the optimal mode is oil treatment in a RPAD within 10 minutes at the rotation rate 10000 rpm. The oil viscosity is reduced from 12,74°VU to 10,93° VU, i.e. by 14,2%.

## 5. Summary

As the result of the comprehensive research performed

the viability of use of natural bitumens of the Nagornoye deposit as the target raw material by production of fuel-oil fractions and bitumens of various application shall be noted.

## 6. Conflict of Interests

The author confirms that the data provided does not contain the conflict of interests.

## 7. Acknowledgments

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