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 bitumes 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 $(HC)^{1,2}$.

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 composition¹. 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 asphaltresinous 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.).

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.	
НК-200°С	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

Table 1. Indicators of the natural bitumen of

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

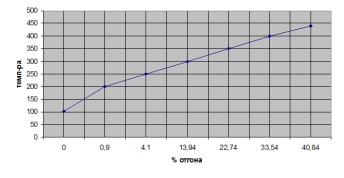


Figure 1. TTC of the natural bitumen from the Nagornoye deposit.

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 distillated 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 distillated 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
productio	on of bituminous

Group	Dependence between content of asphaltenes, resins and paraffin in oil (in % wt.)	Oil fitness for production of bituminous pavements
Ι	A + R - 2,5 P > 8	Most fit
II	A + R – 2,5 P from 0 to 8 At A + R > 6	Fit
III	A + R - 2,5 P < 0 as well as A + R - 2,5 P > 0, 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' oils²⁻⁵.

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^{6, 7} 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 additive⁸ 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 frae	ction distilled up to 350oC

Indicators	For our	GOST 305 for	Test
	product	winter fuel	methods
Fraction composition is			
distilled over at the t, °C:			
50%			
	310	not >250	GOST
96%			2177-66
	350	not >340	
Kinematic viscosity at			
20°C, cSt	1.0	10.50	COCT
	4,9	1,8- 5,0	GOST
Density at 200C leg/m3	026	mat > 940	33-82 COST
Density at 20°C, kg/m ³	826	not >840	GOST 3900-85
Coppor plata tast	With-	Withstands	3900-83
Copper plate test	stands	withstallus	
Flash point	stands	not < 35	
r lash politi		1101 < 55	
(closed cup), °C			
Cloud point, °C	-25	not > (-25)	
Pour-point temperature,	-35	not > (-35)	
°C			
Total sulfur content,		not >0,5	
% wt.			

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	66	20	10
mm, at 25°C			

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 $> 350^{\circ}$ 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

Values
90
80
263
1500
330
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.

Physico-chemical		Mastie	c grade	
characteristics	MBR-	MBR-	MBR-	MBR-
	65	75	90	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

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

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 bitumens⁸⁻¹¹ 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)^{12,13}.

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 itsviscosity.

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

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 RPADprocessingviscosity.

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 pro	cessing

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 fueloil 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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8. References

- Kemalov RA, Kemalov AF. Complex investigations of heavy oil of Akanskoye deposits. Neftyanoe khozyaystvo, Oil Industry. 2012; 10:114-6.
- 2. Kemalov AF, Kemalov RA. Development of the technology of black oil macromolecular structuring in the process of its oxidation for obtaining the bituminous insulating materials. World Applied Sciences Journal. 2013; 23:51-5.
- 3. Kemalov AF, Kemalov RA. Study of disperse polymer systems for producing high-quality polymeric-bituminous materials. Chemistry and Technology of Fuels and Oils. 2012; 48:339-43.
- 4. Kemalov AF, Kemalov RA. Use of natural bitumen as raw

materials for receiving bituminous insulating materials. Neftyanoe khozyaystvo, Oil Industry. 2014, 11, pp. 140-143.

- 5. Kemalov AF, Kemalov RA. Enhancement of interfacial adhesion in bitumen coatings by film-forming agents. World Applied Sciences Journal. 2013; 23:679-84.
- Kamala AF, Kamala RA. Developments of additives the depressor dispersing structures to oil fuels. Proceedings of the 2013 International Conference on the Transformation of Education; 2013. p. 94-105.
- Kemalov AF, Kemalov RA. Creation of chair high-viscosity oil and natural bitumen's at the Kazan Federal (Volga region) University – A step to future competitive technologies of development of heavy oil hydrocarbonic raw materials of the republic of Tatarstan. The Recent Trends in Science and Technology Management, Held by SCIEURO; London. 2013. p. 247-58.
- 8. Soni K. Waste to resource for sustainable development. Indian Journal of Science and Technology. 2016; 9:123-31.
- Kemalov AF, Kemalov RA. Structural and dynamic studies of naphtha crude residue with different chemical nature. World Applied Sciences Journal. 2013; 22:16-22.
- 10. Kemalov AF, Kemalov RA. Relationship between the structural-group composition and physicochemical properties of insulating primers for the protection of oil and gas equipment. World Applied Sciences Journal. 2013; 23:892-7.
- 11. Montazeri-Gh M, Mahmoodi-k M. Investigation of the energy management and power train systems effects on hybrid vehicle performance. Int J of Electric and Hybrid Vehicles. 2015; 7(1):40-61.
- 12. Kemalov AF, Kemalov RA. Scientific practical aspects of receiving bi-tuminous emulsion mastics. Technologies of Oil and Gas. 2012; 6:31-9.
- 13. Kemalov RA. The modified special bitumens and paintwork materials on their basis [Diss. Cand. Eng. Sci.]. Kazan State Technology University; 2003.