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New Generation Wave Technology of Residual Oil-Stock Liquid-Phase Oxidation Process Intensification

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Abstract

In recent years the attitude to bituminous production in Russia significantly changed. In particular, scientific and practical need for naphtha sorting especially for bituminous production is proved. It was promoted by BASHNIYA NP technological classifications of naphtha from the point of view of their suitability for road asphalts production according to which high-paraffinic resinous and paraffinic low-resinous naphtha are recognized unsuitable for production of improved brands road asphalts on the existing technological schemes. Heavy asphaltic naphtha is considered to be the most suitable. The problem of the Heavy Petroleum Residue (HPR) maximal involvement in processing is very timely under conditions of oil products amplifying competition in the market on one hand, and against the increasing requirements to their quality from the point of environment protection view – on the other. Development of scientifically applied bases and the bitumen production technology, applied to road construction, should be noted. Especially it is timely in connection with the bituminous production problems which recently became aggravated sharply in Russia. Timely task for oil refineries (oil refinery) currently is ever growing involvement of high-paraffinic resinous naphtha, with application of raw materials preliminary activation express methods (acoustic exaltation, rotor hydrodynamic source of mechanical oscillations, wave influence) in production of receiving oil oxidated asphalts of improved quality.

Keywords: Bitumen, Heavy Petroleum Residue, Physics – Chemical Properties, Structure, Upgrading, Wave Activation

1. Introduction

For raw materials of bituminous production[1-3] in modern oil refineries tars of various naphtha, cracking oddments, extracts of the solvent oils refining, de-asphaltizing process asphalts, fuel oil, pyrolysis process pitches, are used. It results in need of efficient regulation, both properties of raw materials, and parameters of bitumen manufacture process with the given complex of operational properties[4-6].

2. Experimental Part

For a choice of petroleum refining optimum option there are various classifications of naphtha reflecting their chemical nature. So, the classification reflecting possibility of naphtha use for bituminous production according to which all naphtha are divided into three groups depending on the content of asphaltenes, pitches and paraffin, for bituminous production heavy asphaltic naphtha is offered, and, the more the relation of asphaltenes to pitches are considered as optimum raw materials, the higher is the quality and exit of the received bitumen. The most prime and economic production technology of bitumen is receiving residual asphalts. Suitability of naphtha for residual asphalts production can be estimated on Bitumen yield (B) with depth of needle permeating at 25°C 100·0.1 mm which correlates with naphtha capability volume (K): $B = 4.9 \cdot K^4$. It is considered that production of residual asphalts is economically expedient if their exit makes no less than 10-20% mass.

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Table 1. Physical and chemical properties of naphtha mix.

Value Name	Devonian and Carboxylic naphtha of JSC Taif-Oil Company	Romashkinsky and Kama fields of PJSC Tatneft
1. Density, at 20°C, kg/m^3	900,7	918,9
2. Kinematic viscosity, mm^2/s: At 20°C At 50°C	87,15 20,73	189,8 41,9
3. Content in naphtha, % mass.: Water Of sulfur Paraffin Pitch Asphaltenes solt, mg/l	Trace 2,0 2,22 20,20 2,60 9,6	Trace 4,0 8,3 22,6 4,2 13,1
4. Fractional composition, %: c.n. – 100°C 100 – 200°C 200 – 300°C 300 – 350°C	5,2 10,8 15,5 8,2	4,0 8,6 16,0 7,6
5. Freezing point, °C	-12	-19
6. Flash point, °C	7	25

Table 2. Physical and chemical properties of fuel oil mix.

Value Name	Devonian and Carboxylic naphtha of JSC Taif-Oil Company	Romashkinsky and Kama fields of PJSC Tatneft
1. Density, at 20°C, kg/m^3	955,2	1003,6
2. The funnel viscosity, sec. at 60^{0}C at 80°C	–20,20	136,8 30,7
3. Flash point, °C	230	265
4. Softening point by KISh, °C	27,2	31,5
5. Cokability, %mass	9,51	13,5
6. Content, % mass. sulfur asphaltenes Pitch	2,39 2,97 31,6	traces of 4,5 7,6 56,5
7. Fractional composition, %: c.n. – 3000C	n/a	n/a
8. Boiling temperature °C	350	300

Currently in Russia the dominating method of receiving bitumen for roads is processing liquid-phase high-temperature oxidation of heavy petroleum residue[4]. Let us note that chemical composition of initial oil-stock and ways of its processing have essential impact on operational properties of the received bitumen. Ratios of the naphtha and fuel oil mixture received from them are presented in Table 1 and Table 2.

As raw materials of oxidation process in the real work fuel oil of naphtha mix of Romashkinsky and pre-Kama fields of JSC TatNeft, which physical and chemical properties are presented to Table 2, was chosen.

In recent years some researchers established that the long-lived radiation destructively affects the majority of known organic materials. Therefore there was a need for operational properties research of such materials as plastic, coverings and bitumen for electromagnetic radiation zone and their ability to resist its influence. Influence of electromagnetic radiation on organic compounds is actively studied[5,6], for the purpose of electromagnetic oscillations influence definition on bituminous materials, mainly on asphalts recently, and to use the obtained data in practice. Bituminous materials considerably differ among themselves by structure, which depends on a source of raw materials and a way of receiving materials[7-9].

Table 3. Characteristics of the ENPU (350^{0}C) temperature-controlled fuel oil.

Index Name	Value		
	10 min.	15 min.	20 min.
Density, at 20°C, kg/m^3	936,2	946,7	956,4
Viscosity VU_{80}	4,23	6,28	7,6
Contents fr., ^{0}C: c.n. -105 105-120 120-150 ***Total*** 150-190	% , mass. 0,2 0,35 2,5 ***3,05*** 1,8	% , mass. 0,63 0,28 2,7 ***3,61*** 3,5	% , mass. 0,8 0,2 3 ***4*** 4

Change of group chemical composition and structure of heavy oil residue exemplars, confirmed by the gradient of density and viscosity indexes, before wave influence is first of all result of electromagnetic field impact on the studied raw materials. Characteristics of temperature-controlled fuel oil at 350^{0}C within 10, 15, 20 minutes shown in Table 3, after electromagnetic field influence within 2 hours at a temperature of 210^{0}C, depending on activation time (at 350^{0}C) are presented in Table 4. At impact on fuel oil of fluctuations with frequency of 72.2 kHz there is an exaltation of hydrogen atoms contained in various molecules. Characteristics of Elkhovsky NPU PJSC Tatneft (ENPU)

Table 4. The characteristic of ENPU fuel oil after electromagnetic field influence (2100C, 2 hours).

Index Name	Value
1. Density, at 20^{0}C, kg/m^3	922,3
2. Viscosity VU_{80}	3,35
3. Contents fr., °C: c.n. -105 105-120 120-150 ***Total***	%, mass. 0,12 0,36 2,72 ***3,2***

fuel oil after electromagnetic field influence within 2 hours at a temperature of 210^{0}C are presented in Table 3 and 4.

In our opinion, decrease in density from 1003,6 kg/m^3 to 922,3 kg/m^3, and viscosity VU_{80} from 7,04 to 3,35, is caused by formation of the light fractions which are boiling away to 350^{0}C (3,2% mass) formed as a result of destruction processes, cracking reactions of the activated, exited raw materials. In fuel oil thermo-stating at 350^{0}C within 10, 15, 20 min., after influence of electromagnetic field, there is an increase in density (from 922,3 kg/m^3 to 956,4 kg/m^3) and increase in viscosity VU_{80} 3,35 to 7,6 respectively that is caused, on one hand, by slight destruction processes of heavy hydro-carbonic part (confirmed by gain in yield of light fractions to 190^{0}C), on the other hand, there are reactions of consolidation, "gumming". Thus, it is possible to assume the restitution of supermolecular structures in a disperse system, in the absence of hashing. Fractions existence having decomposition temperature 190^{0}C in fuel oil, which is lower than their final boiling point, should be noted.

It is revealed that the mass contents of light and low-boiling fractions increase twice for the account decrease the fraction maintenance above 420^{0}C. During raw materials oxidation to bitumen many reactions with various constants of speeds proceed. With oxidation temperature increase the speeds of oxidizing reactions are accelerated. Depending on the nature of raw materials and the demanded properties of bitumen it is necessary to select the corresponding temperature of oxidation. At a temperature below 210°C speed reactions are small and time of raw materials oxidation becomes long. At temperatures above 280°C reactions of carbines and carbides formation prevail, thus worsening bitumen quality. Therefore in practice of oxidation for the majority of raw materials types taking into account economic feasibility it are close to 250°C. In the course of oxidation temperature of process and air consumption were supported in the range of 240-260^{0}C and 3l/min*kg raw materials, respectively.

Table 5. Changes of physical and chemical properties of the ENPU initial fuel oil during oxidation.

Index Name	Time of Oxidation, Min			
	120	**240**	**420**	**600**
1. Depth of needle permeating, 0,1 mm: - at 25°C; - at 0°C	>350	>350	202	90
2. Softening point on ring and sphere, °C	36	39	42	44
3. Brittleness temperature, °C	–	–	–21,8	–35,9
4. Flash point, °C	230	230	240	240
5. Tensile properties, cm - at 25°C; - at 0°C	11,5	16,0	20	18,5
Penetration index	–	–	0,87	–1,4
6. Coupling with marble or sand	3,0	3,0	3,0	3,0
7. Change of softening point after warming up, °C	–	–	2,8	3

As a result of the physical and chemical properties analysis, the most prime dependence is traced between time and softening point during oxidation. It is established that softening point increases with increase in concentration of asphaltenes in oxidates. Depending on the content of asphaltenes bitumen represent the colloid systems having sol, sol-gel, and structure gel which destruction requires different energy. Bitumen with high content of asphaltenes possesses structure of gel and has higher softening temperature. It is known that at high values of softening point with increase in penetration and ductility bitumen quality increases. The tensile properties at first increase in the first seven hours of oxidation, then they decrease shown in Table 5.

Thus, percentage of asphaltenes, due to reduction of oils and pitches increases. For initial fuel oil asphaltenes increase due to initial accumulation of pitches.

Dependence of small co-metric properties from the fuel oil oxidation time before hand activated by electromagnetic oscillations at a temperature of 150^{0}C and 210^{0}C is presented on Figure 1 and Figure 2.

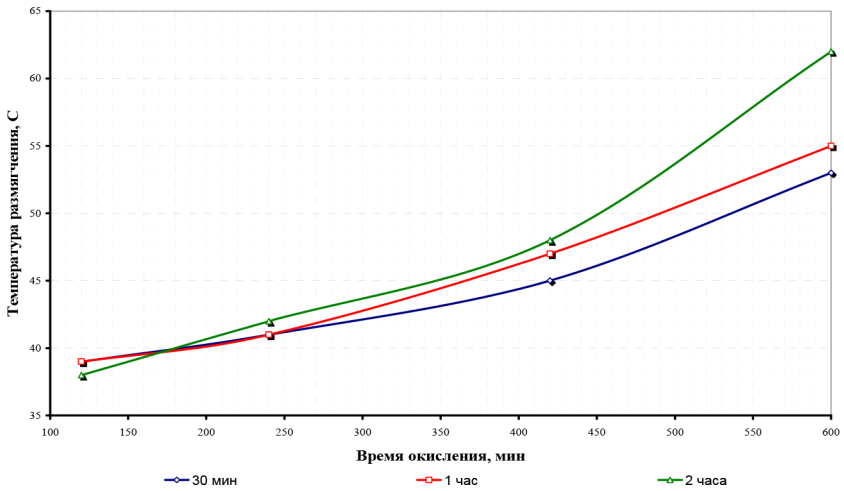


Figure 1. Dependence of softening temperature from fuel oil oxidation time beforehand activated by electromagnetic oscillations at a temperature of 150ºC.

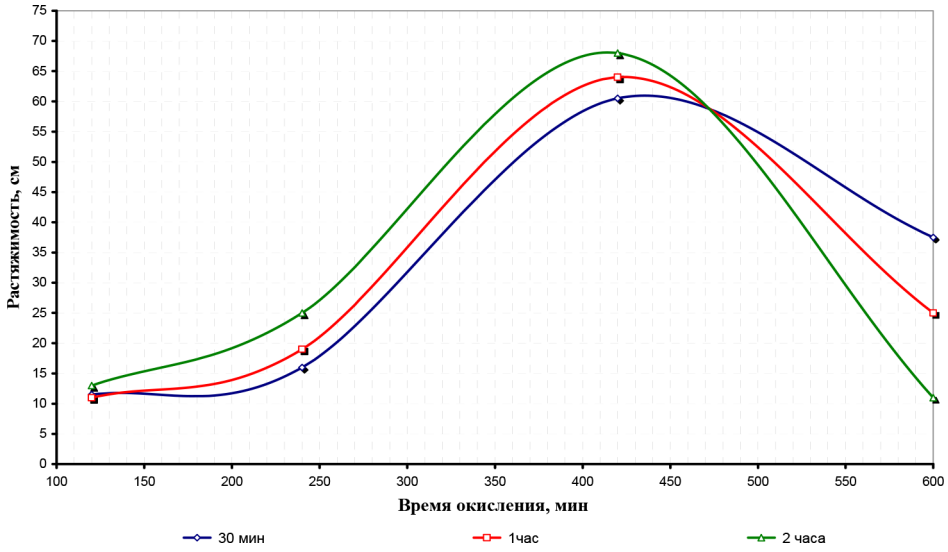


Figure 2. Dependence of expandability from fuel oil oxidation time beforehand activated by electromagnetic oscillations at a temperature of 150ºC.

An interesting dependence of physical and chemical bitumen properties takes place during oxidation. It should be noted that the increase in softening point during the first hours of oxidation probably is bound to accumulation of pitches, confirmed by the sharp increase in tensile properties, thus concentration of asphaltenes changes not considerably, and then gum content on extent of all oxidation process remains constants shown Figures 3 and 4.

The changes in properties of bitumen during 10 hours oxidation are caused, in our opinion, by the structural changes taking place in oxidation of heavy petroleum residue.

Dependence of brittleness temperature and penetration of oxidates over time process more composite as these indexes depend more on properties of dispersion medium – oils and pitches. On one hand, brittleness temperature of oxidates, as well as softening point, increases with increase in the content of asphaltenes and their sizes that leads to forming a rigid framework in bitumen, its hardness increases[10-12]. On the other hand, brittleness temperature increases owing to weakening of dispersion medium that increases junction temperature of bitumen in solidity. The penetration, which is viscosity parameter,

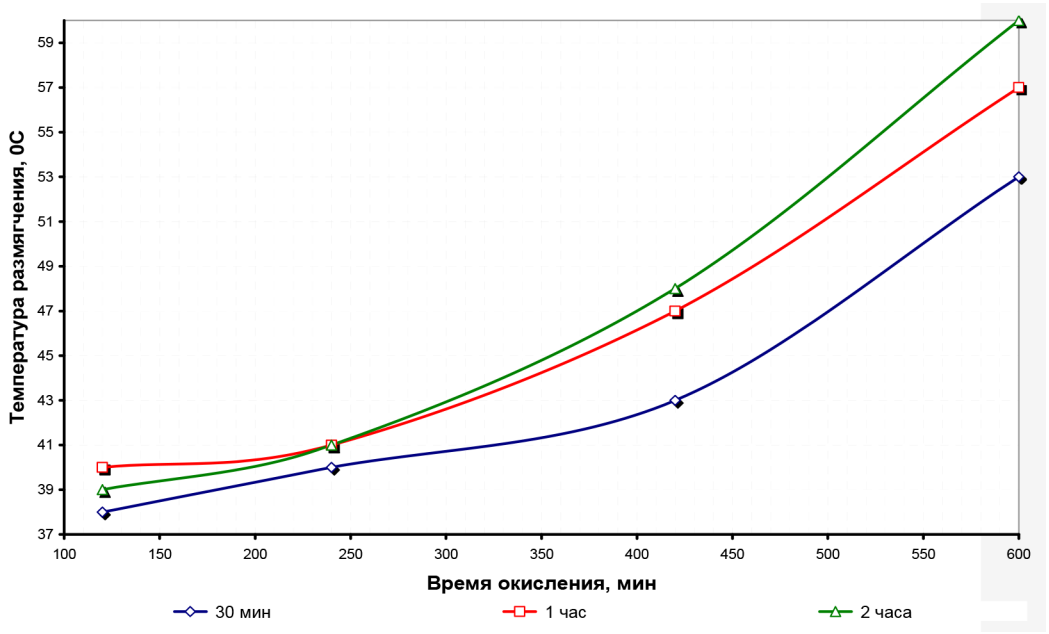


Figure 3. Dependence of softening temperature from fuel oil oxidation time beforehand activated by electromagnetic oscillations at a temperature of 210ºC.

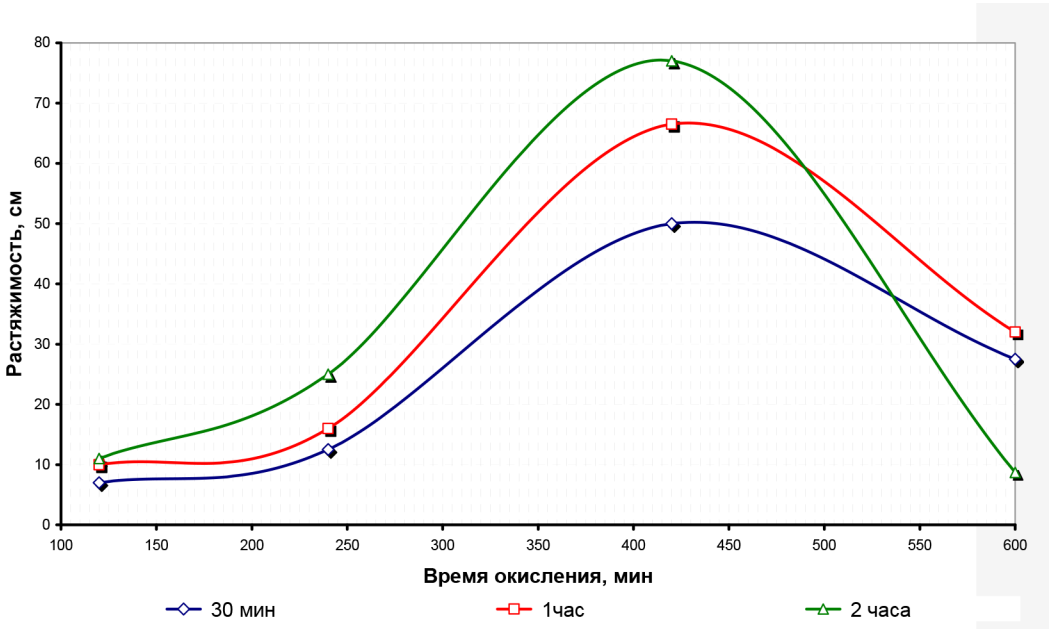


Figure 4. Dependence of expandability from fuel oil oxidation time beforehand activated by electromagnetic oscillations at a temperature of 210ºC.

also characterizes change of bitumen plasticity depending on change of its group chemical composition.

At comparison of activation effectiveness depending on temperature and time it is possible to establish that the most acceptable condition of carrying out activation of ENPU fuel oil are 150°C, 120 min. The comparative analysis of operational properties of the received oxidated asphalts from initial raw materials, ENPU fuel oil (exemplar 1), and also the activated fuel oil (respectively exemplars 2, 3 and 4) was carried out according to the

Table 6. Indexes of received oxidated asphalts quality.

Index Name	Measure Values						
	GOST 22245-90	EN 12591	Exemplars 600				
	BND 60/90	Brand 70/100	No. 1.	No. 2.	No. 3.	No. 4.	
1. Depth of needle permeating, 0,1 mm: - at 25°C; - at 0°C	61-90 No less than 20	70-100 -	202	84	89	87	90
2. Softening point on ring and sphere, °C	No less than 47	43-51	42	48	48	48	44
3. Brittleness temperature, °C	No higher than -15	– 10	-21,8	-24,8	-18,3	-21,6	–35,9
4. Flash point, °C	No less than 230	No less than 230	240	240	240	240	240
5. Tensile properties, cm - at 25°C; - at 0°C	No less than 55 No less than 3.5	–	20	68	57	77	18,5
6. Coupling with marble or sand	–	–	3	2,5	2	2	3,0

main requirements imposed to bitumen shown in Table 6. The analysis of physical and chemical bitumen properties was carried out by periodic sample drawing from oxidizing installation in oxidation process. Normative requirements to road asphalts in Europe within the uniform EN 12591 (for bitumen with a penetration values range of 70/100) standard are provided in Table 6. Comparative characteristics of the road bitumen appointment received by oxidation of the activated ENPU fuel oil on compliance with indexes of GOST 22245-90 are provided in the same table. As a result of the conducted researches, exemplars of the received by activated ENPU fuel mix bitumen according to the qualitative characteristics, namely softening point, depth of needle permeating, fully conform to the standard, and on separate indexes, such as tensile properties and brittleness temperature, surpass requirements of the above standard. According to the obtained data the common tendency of bitumen properties improvement received by oxidation activated fuel oil is planned[13,14]. At identical values of softening point the penetration goes down, brittleness temperature considerably does not change. The common tendency of increase in softening point is explained by non-additive interactions in system with hydrogen bridges formation between the functional groups of R-H and atoms (the same atoms groups or another molecule). Thus, relation is established R-H…R_1. The hydrogen bridge is formed by electrostatic and donor-acceptor interaction of bitumen components with polar bitumen components, appeared as a result of electromagnetic influence.

The solvates and associates, which are formed thus, lower the common energy of system that leads to softening point increase. On one hand, thermal stability of bitumen should not be below the maximal running temperature (surface temperature of highways in summertime makes 70°C), on the other hand, high softening temperature complicates their application as binding in asphalt concrete mixes (bitumen with high softening temperature, and, therefore, high viscosity badly envelop mineral filler surface).

3. Summary

The received results on combination of electromagnetic activation and oxidation processes open prospect of feed stock choice optimization for oxidation and oxidation technology. It is possible that electromagnetic activation will allow receiving qualitative road asphalts from raw materials having the high content of paraffin durums.

4. Conclusion

Activation of fuel oil allows creating conditions in the course of oxidation under which the relative frame of non-coupled conduction electrons in the colloid particles of bitumen are almost completely localized, which leads to their stabilization. Coagulation and loss of asfaltene fraction crystals when aging in this case is strongly kinetically and sterically complicated and, for the most part, does not happen.

5. Conflict of Interest

The author confirms that the presented data do not contain the conflict of interests.

6. Acknowledgments

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