Structural and Dynamic Studies of Naphtha Crude Residue with Different Chemical Nature

Alim Feizrahmanovich Kemalov and Ruslan Alimovich Kemalov

Kazan (Volga Region) Federal University, Kazan, Russia

Abstract: It is known that the tars of heavy oils of naphthene-aromatic base with high concentrations of resin-asphaltene substances (RAS) and insufficient content of high-molecular paraffins are the most suitable raw material for production of a wide range of bituminous products in general and bituminous insulating material (BIM). Naphtha crude residues (NCR) of paraffin and high-paraffin crude oils are usually used due to limited oil production. It is notable that the production of refractory special bitumens at high-temperature oxidation of residual materials results in production of non-hydrocarbon compounds - carbenes and carboides that are insoluble in hot benzene, as well as the compounds of paraffin-naphthenic base containing in extracted oil. Considering the NCR as a thermodynamic system of phases *A*, *B* and *C*, it should be noted that the structure of carbon links of phases can be assumed by evaluation of molecular mobility and structural-dynamic parameters. Structural-dynamic states of NCR at different temperatures were studied using relaxometer NMR 08BK/RS and used as raw material for oxidation.

Key words: Naphtha crude residues % Paraffin-asphalt associates % Physical-chemical modification % oxidative polymerization % Structurally complex links % Nuclear magnetic resonance relaxation (NMR-relaxation) % IR - spectroscopy

INTRODUCTION

According to the studies of A. Kolbanovskii [1-9], the dispersed structure of bitumen is largely determined by the content of straight-chain paraffinic hydrocarbons (HC) [10]. Crystalline skeleton of paraffins occurs at HC concentration higher 3% which stretches the hardness and reduces plasticity that negatively affect the physical and mechanical properties of BIM. Thus, the refinery of NCR with paraffin-naphthene base results in their activation by modifiers which undergone the segments of paraffin chains the chemical structuring followed by formation of macromolecular polycyclic naphthene-aromatic fragments due to effective intermolecular diffusion during oxidation.

It is known that the influence on the supramolecular structure of the magnetic, electromagnetic and acoustic fields, as well as an introduction of various additives to the NCR allows the change of the size of the dispersed phase in the wide range and directed control of the properties [10-20]. It was found that this effect is achieved by adjusting the size of the oil dispersion systems (ODS), which core is a gas bubble during oxidation. Syunyaev Z.I., Apostolov S.A., Kemalov A.F.,

et al. [4-6] found that the disperse state of NCR influences the reaction speed and quality of bitumen. This fact has not previously been taken into account for optimization of bitumen production technology and insufficiently studied.

Using this approach, the structure of NCR during oxidation has to acquire high-resin type and the oxidation results in formation of the structures with chemical composition similar to asphaltenes but possessing the physical-chemical properties of the "heavy" resins. As a result, the obtained sample of special bitumen characterizes by high content of film-forming agent – the resin with low amount of paraffin structures and asphaltenes.

To determine the effect of NCR chemical structure on oxidation kinetics, physical and mechanical properties of BIM and taking into account the results of our previous studies evidencing that oxidative polymerization is accomplished at the stage of construction bitumen synthesis, the tars of naphthene-aromatic (Karabash Oil-Bitumen Plant (KOBP) – tar-1) and paraffin-naphthene bases (Elkhovskiy Petroleum Refining Plant (EPRP) OAO "Tatneft" – tar-2) served as the raw material for production of special bitumen (Table 1).

Corresponding Author: Kemalov, Kazan (Volga Region) Federal University, ul. Kremlevskaya 18, Kazan, 420008 Russia.

Table 1: Physical and chemical properties of tars

Parameters	Tar-1	Tar -2
Density, kg/m^3	0,9686	0,9878
Relative viscosity, RV_{80},	22,96	51,76
Content, % wt.:		
- resinous-asphaltenic substances	18,25	28,23
- scrape	0,492	0,887
- paraffins	less 2,00	15,00
Asphaltene / resins	0,64	0,45
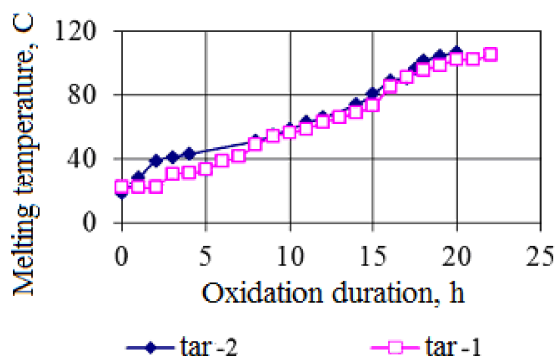
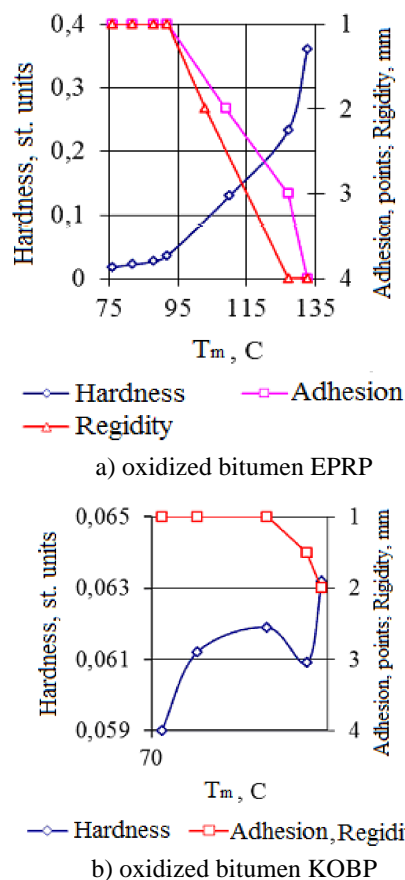Fig. 1: Dependence of T_m of bitumens on oxidation duration

Oxidation of tars was carried out on a laboratory batch operation installations at 250°C and air flow 3 l/min*kg of raw material.

Studies of the general physical and mechanical properties of bituminous varnishes prepared using special bitumens have showed the ambiguity of their evaluation (Fig. 2). Thus, coatings (C) based on oxidized tar-2 characterizes by high hardness - 0.36 st. units (Fig. 2a) and low adhesion-rigidity properties. Moreover, C based on special bitumen KOBP with T_m 110°C characterizes by lower hardness 0,0619 st. units and high adhesion-rigidity properties (Fig. 2b).

This can be explained by high content of paraffin-naphthene hydrocarbons and asphaltenes in tar-2 compared with tar-1 (Table 1).

There was direct proportionality between the content of paraffin hydrocarbons and asphaltenes and the density and relative viscosity of tars found. High content of total sulfur in the raw material during oxidation results in transformation of colloidal disperse system, i.e. an increase of the content of the dispersed phase – asphaltenes and reduction of dispersion medium – petrolene part which is film-forming base of BIM.

It should be noted that the investigated tars (Table 1) with different physical-chemical properties characterize by different concentration of sulfur and dispersed phase.

a) oxidized bitumen EPRP

b) oxidized bitumen KOBP

Fig. 2: Dependence of physical and mechanical properties of BIM prepared using oxidized bitumens on T_m.

At the same time, the study of oxidation kinetics (Fig. 1) shows the similar reaction rate that results in synthesis of refractory bitumens (KOBP and EPRP) with T_m 80–130°C, whose BIM characterize by different physical and mechanical properties.

The solution of the identified contradictions requires the study of the relationship between physical and chemical nature of the crude material, methods of its modification and properties both oxidation products and final products. In this regard, it is necessary to use the study methods, which, considering the complexity of the chemical composition of raw materials will ensure the reactivity and properties of the final product.

Nuclear magnetic relaxation [1, 8, 10], which is a fundamental property of nuclear magnetism, characterizing the dynamics of system of nuclear spins in tars, bitumens, etc. belongs to the modern instrumental physicalal chemistry methods for investigation of newly formed equilibrium structures. High comprehension of

nuclear magnetic relaxation parameters on the properties of studied substance, relative simplicity of the experimental determination of these parameters, as well as the reliability of the theoretical interpretation of the data can determine it as an independent physical method of investigation.

Study of mobility of the molecules and atoms in solid bodies, liquids and gases, the study of complexation reactions, chemical exchange, solvation and intermolecular interactions in solutions, the definition of the parameters of the electronic structure of metals and alloys, the study of electron-nuclear interactions, structure and properties of molecules are incomplete range of tasks which can be solved by NMR spectroscopy. This method is attractive both for physicists and chemists and for experts in the field of technology, what is stipulated by the practical significance of the NMR data which processes are dependent on numerous physical and chemical properties of the studied system and clear indicate the dynamic activities at the molecular level.

Studies of ODS by NMR relaxometry are conducted deriving from single complex structural unit (CSU), that is, studying the temperature influence at changing of the thermodynamic characteristics of the spin-spin system, the the structural features of ODS can be supposed in general.

According to the Karr-Purcell-Meiboom-Gill method, the activity of the magnetic field and alternate magnetic impulses, affecting the magnetization of the nuclei occurs in the spin system that they process with a certain frequency of oscillation amplitudes, i.e. molecular mobility of paramagnetic nuclei is increasing. This phenomenon is expressed by *spin-spin relaxation time T_{2i}*.

In particular time and constant temperature of the experiment (T_{exp}), the magnetization saturation of the phase[1] nuclei reaches the constant discretion that result in "exchange" of nuclear magnetization with surrounding spin systems. This increases the molecular mobility of the most active links of the studied phases. Registered thermodynamic "response" (TDR) of adjacent ODS is expressed by segmental precession or amplitudes of oscillation frequencies of the most active magnetic nuclei and called as the *time of spin-lattice relaxation T_{1i}*. The spin-lattice system of phases i in NMR spectroscopy serve as a group of spin-spin systems Gi.

It should be noted that the TDR of the spin-lattice system is overlapped by precessions of the magnetic nuclei of the structural links which characterize by the spin-spin relaxation time T_{2i}. This phenomenon consists in the fact that studied ODS is affected by a constant magnetic field, alternate electromagnetic impulses and T_{exp}. As a result, there is direct proportionality between the time of spin-spin and spin-lattice relaxation in the CSU and ODS, respectively.

In this regard, the presence of a constant magnetic field in the study of structural and dynamic parameters in the NCR is explained by the obligatory presence of equality of values of the spin-spin relaxation time T_{2i} in ODS, located in one of the phases. Otherwise, the effect of an alternate magnetic field will change the TDR by reducing T_{2i} and as a result, T_{1i} will tend to zero (T_{1i}60).

Thus, the extremes TDR in ODS will occur in most mobile phases **A** and **B**, i.e. $T_{1A} > T_{1B} > T_{1C}$.

Possible structural–dynamic states of ODS at the initial time at $T_{exp} = t_{in}$.

Knowledge of the structural and dynamic parameters, the state of thermodynamic stability of RAS in ODS allow us characterize it using "express analysis", i.e. the data of NMR relaxometry of initial state of the oil system will allow us the conclusions on the theoretical background of its physical-chemical, thermodynamic activity at the destructive thermal treatment. Thus, the type of segmental structure of the carbon chain can be determined using the values of the amplitudes of oscillation frequencies of magnetic nuclei and occupancies of surrounding hydrogen protons.

Using the system (I) shown in Table 2, we can assume that the response of P_{1A} is a result of the most active substituted alkyl chains (mainly short-chain, which can be methyl and ethyl substitutes). However, the low values of T_{2A} and T_{1A} indicate the steric obstacles in carbon chain as the reason of the response. Thus, the main character of the segmental structure of phase **A** characterizes by long-chain paraffin structure of the links.

It should be noted that the obstacles in determination of degree of substitution and an aliphatic chain length of phase A in the initial time are caused by its "frozen" condition. At high T_{2A} and P_{2A} (II) and aligning it with the data for P_{1A} and T_{1A} where response $P_{1A} \sim P_{2A}$ (or insignificantly lower), the structure of substitutes of phase **A** can be characterized with a certain degree of probability, as the short-chain structure with high degree of branching.

---

[1]**Phases** – the parts of the system with identical chemical composition, physical and thermodynamical properties, characterized by different molecular mobility determined by structural-dynamic analysis (SDA).

Table 2: Structural-dynamic states of ODS in initial time at $T_{exp} = t_{in}$

Type of system	Structural-dynamic characteristics of spin-spin system	Level of TDR in ODS
(I)	T_{2A} – small quantity	$T_{1A} \sim T_{2A}$ (or slightly higher)
	P_{2A} – high (~80% wt.)	$P_{1A} > P_{2A}$ (up to 40-50%)
(II)	T_{2A} – high	$T_{1A} \sim T_{2A}$ (or insufficiently higher)
	P_{2A} – high (~80% wt.)	$P_{1A} \$ P_{2A}$ (up to 50-70%)

Table 3: Characteristics of covalent bond

Bond	Type of hybridization of carbon atom	Bond length, nm	Angle between the hybrid orbitals	Binding energy, KJ/mol	Shape of molecule
C–C	sp^3	0,154	109°28`	350	tetrahedral
C=C	sp^2	0,134	120°	605	planar
C=C	sp	0,120	180°	825	linear

The presence of the alkyl double bonds in carbon chains can be determined using the values of T_{2A} and P_{2A} and taking into account the fact that the length of C=C bond is less than C–C and binding energy (Table 3) of $\star_{C=C}$ is greater $\star_{C-C}$. This is confirmed by the fact that an increase of number of C=C double bonds results in drastic reduction of T_{2A} values and, thus, T_{2A} will close to T_{2A} and P_{2B} will characterize by lesser values. However, the values of T_{1A} may be significantly lower T_{2A} because the double bonds in NCR stipulates "ordering", i.e. has a tendency to further intermolecular structuring.

Considering NCR as a thermodynamic system of phases *A*, *B* and *C* it should be noted that the structure of carbon links of phases can be determined considering their molecular mobility and structural-dynamic parameters.

Previously, it was found by dynamic structural analysis (SDA) that ODS contain phases *A*, *B* and *C*, which, due to their different content and molecular mobility are conditionally considered as the oils, resins and asphaltenes, respectively.

Study of Structural-dynamic Parameters of Tars Different Chemical Nature by Impulse NMR: Structural and dynamic states of NCR were studied as material source for oxidation using relaxometer NMR 08BK/RS at different temperatures as a raw material of the oxidation process were studied at different temperatures.

The tars were analyzed in following regimes: launch period T = 500 µs – 2 s, the interval between 90°and 180° impulses N = 5 – 1000 and number of accumulations n = 3 – 50. The time of analysis did not exceed 3 min.

According to Figure 3, a rectilinear correlation between T_{exp} and relaxation time T_{2i} was observed i.e. $10^3/T$ is directly proportional to T_{2i}, however, T_{2C} for tar-1 was significantly different from T_{2C} for tar-2.

Figure 3 shows the insufficient differences in molecular mobility of the components in studied tars, characterized by the spin-spin relaxation time T_{2i}. However, a more detailed comparative analysis of the experimental data shows that T_{exp} which reveals phase *C* is different for each tar: 72°C for the tar-1 and 49,6°C for tar-2.

High T_{exp} which reveals phase *C* is explained by steric obstacles of mobility of the molecular structure i.e. tar-2 possible characterizes by more ordered molecular structure of asphaltenes than tar-1.

Figure 3a shows that relaxation time T_{2C} is not significantly changed for tar-1 during whole interval T_{exp} that indicates a thermodynamically stable structure mainly composed of links (segments) of polycyclic naphthene-aromatic structure with low degree of substitution by alkyl chains.

Comparative analysis (Fig. 3) has shown that increase of T_{exp} above 60°C, molecular mobility of substituted links of phases *C* also increase with different degree. This is caused by both structure of dispersed phase and degree of substitution, branching and length of chain of substitutes. Impulse NMR showed that substitution pattern of phase *C* is expressed by long alkyl chains with insufficient branching what is confirmed by occupancies of protons P_{2C} (Fig. 4), which shows the low concentration of the phase *C* in tar-1 (up to 20% wt.). Thus, the comparative analysis of the structural-dynamic parameters of the tar indicates the presence of insignificant aromaticity and high content of paraffin-naphthene hydrocarbons in tar-2.

Analysis of dependencies T_{2A} and T_{2A} from $10^3/T$ (Fig. 3) shows that the time T_{2A} for tar-2 is 2,5 µs, what significantly exceed time T_{2A} for tar-1 – 0.65 µs. At the same time, T_{exp} which manifests mobile phase *A* for
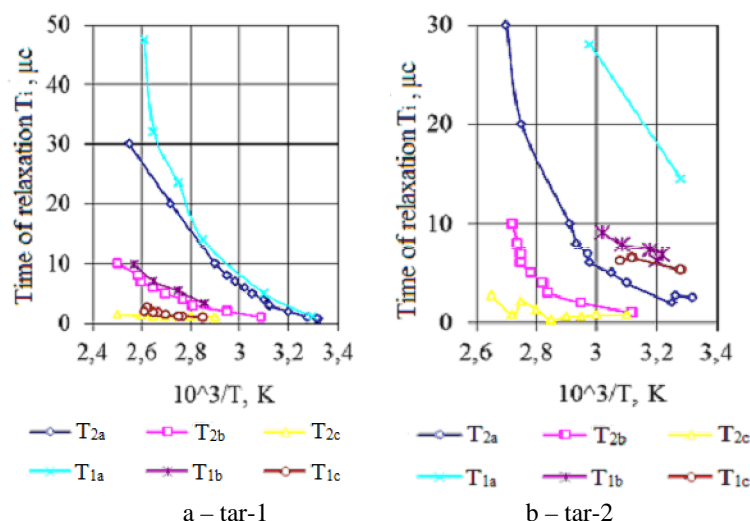
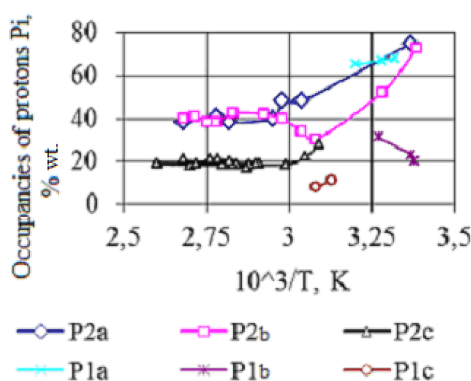Fig. 3: The temperature dependence of relaxation time for tars

Fig. 4: The temperature dependence of the occupancies of protons of phases in tar-2.

tar-1 is 28,2°C and 31,8°C for tar-2. It is important that at similar T_{exp} 10^3/T for both tars – 3,28 Б, different relaxation times T_{2A} are observed: 1 µs for tar-1 and 2,5 µs for tar-2.

It should be noted that at 72°C>T>55°C, T_{2A} for tar-1 is higher then for tar-2 in average by 8% wt. However, inverse relationship at T>72°C explained by phase transitions (PT) related with structural-dynamic transformation of molecular morphology was observed. Thus, it can be concluded that the most mobile phase A of tar-2 is characterized by a long-chain paraffin links and for tar-1 by short-chain aliphatic links which on our opinion are the structural segments of a high molecular part of the dispersion system and respectively, less mobile - resins characterized by T_{2A} relaxation time.

According to the data on molecular mobility of phase B, it was found that relaxation time T_{2A} for tar-1 is less than the tar-2 within the whole interval 10^3/T.

This characterizes the chemical structure of phase B in studied NCR, which, as we assume, mostly consists of polycyclic naphthene-aromatic structures in the tar-1 and phase B in tar-2 characterizes by polycyclic paraffin-naphthenic structures, what is also confirmed by the time of spin-lattice relaxation T_{1i} (Fig. 3) and occupancies of protons P_{1i} (Fig. 4).

Thus, found differences in the relaxation times of the most mobile phases T_{2A} and T_{2A} for both tars confirm the high content of paraffinic structures in tar-2 (Table 1), which is a significant disadvantage in the production of BIM (Fig. 2).

The study of most mobile phases A and B - P_{2A} and P_{2A} shows symbasis of graphical dependencies (Fig. 4). In the initial time, the measurements in the interval T_{exp} – 10^3/T 3,13–3,16 Б, P_{2A} for tar-2 (. 47,5% wt.) significantly exceeds the value of proton's occupancies for tar-1 (. 62% wt.) and observed hopping alteration of P_{2A} for tar-2 stabilizing at 55°C until 50% wt. insignificantly varies within 40% wt.

Alteration of the occupancies of protons P_{2C} (Fig. 5) indicates that the phase C of tar-1 is represented by polycyclic naphthene-aromatic structures and Fig. 5a shows that P_{2C} characterizes by thermodynamic instability in contrast to P_{2C} for tar-2 (Fig. 4) expressing by extremes of dependence of P_{2C} on 10^3/T. Thus, there is high chemical resemblance of phase C with resin components.

Comparison of thermodynamic "response", i.e. the ratio of time T_{1i} to occupancies of protons in lattice P_{1i} with occupancies of protons P_{2i} in studied NCR and evaluation of the activation energy (E_A) allow the
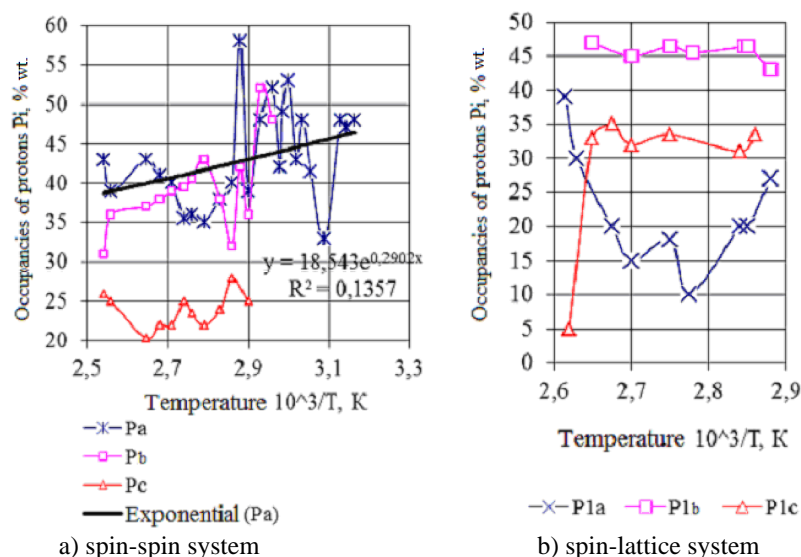
a) spin-spin system

b) spin-lattice system

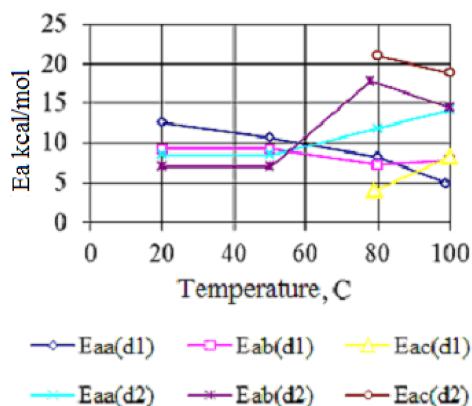Fig. 5: Dependence of occupancies of protons of phases P_i of tar-1 on temperature

Fig. 6: Dependence of activation energy on temperature

assessment of segmental thermodynamic activity of lattice elements using P_{1i} values and characterize the ordering degree of spin-lattice system. The study of spin-spin system of magnetic nuclei of NCR and parameters of T_{1i} and P_{1i} using T_{2i} and P_{2i}, reveals the quantitative distribution of the phases in spin-lattice system.

E_A values of the molecular motion in Arrhenius' assumption for time of correlation $J_c = J_0 \exp(E_A / RT)$ were obtained using the formula (1):

$$E_A = 19,13\left[T^{(1)}T^{(2)}\Big/(T^{(2)} - T^{(1)})\lg\left(T_2^{(2)}\Big/T_2^{(1)}\right)\right] \qquad (1)$$

where $T^{(1)}$, $T^{(2)}$ – the temperatures at which relaxation times $T_2^{(2)}$ and $T_2^{(1)}$ have been determined.

At that, only intramolecular input to relaxation stipulated by dipole-dipole interactions of rotational diffusion, which are accomplished for ODS at high-temperature approximation $ωJ_0 \ll 1$, is taken into account for protons with spin $I = ½$ is:

$$(T_{2BH})G^1 = 3\left(^4h^2J_c/2r^6\right) \qquad (2)$$

In this regard, graph dependences of time of spin-lattice relaxation T_{1i} for tar-1 are located in the plane-parallel direction according to dependences of spin-spin relaxation T_{2i} (Fig. 3) as well as the occupancies of protons P_{1i} are parallel to each other. The presence of extremes (Fig. 5b) for P_{1A} and P_{1C} are explained by the presence of PTs. Increase of time T_{1C} within the temperature range 2,6–2,755 can also be caused by the presence of PT related with structural and dynamic rearrangement of the molecular morphology and involvement into the molecular mobility of phase *C* of some structural links in resin molecules with higher chemical affinity.

The results of the analysis (Fig. 6) of dependences of E_A on T_{exp} for tars are agree with the results of NMR relaxometry and entirely confirm our previous assumptions on possible chemical structure of the ODS components of tars. Figure 6 shows that activation energy in tar-1 is higher at low T_{exp} and lower at higher T_{exp} then in tar-2. The maximum E_A are close to the values specific for potential barriers at steric obstacles of molecular

motion of long-chain polymers such as polyethylene with E_{Apol} . 12–14 kcal/mol [10]. E_A for tar-2 depending on T_{exp} is characterized at low T_{exp} by "frozen" state of long aliphatic chain segments and high mobility terminal and side chains and at high T_{exp} by steric obstacles in molecular segmental mobility.

CONCLUSIONS

Thus, the results of the analysis of structural and dynamic characteristics of initial NCR show that tar-1 is the most suitable material for production of special bitumen. This is confirmed by NMR relaxometry data, physical-mechanical properties of BIM and special bitumens produced using BIM. However, the analysis of naphthene-aromatic base of tar-1 characterized by low branching of the terminal groups of short-chain aliphatic substitutes showed that its chemical modification during joint oxidation with additives hardly results in required initiation of oxidative polymerization, which is the most favorable for production of high-tensile coatings.

REFERENCES

1. Kemalov, A.F., 2005. Intensification of production of the oxidized bitumens and the modified bituminous materials on their basis, Cand. Sci. (Tech.) Dissertation, Kazan State Technology University.

2. Kemalov, R.A. and A.F. Kemalov, 2012. Scientific Practical Aspects of Receiving Bituminous Emulsion Mastics. Technologies of Oil and Gas, 6: 31-39.

3. Kemalov, A.F. and R.A. Kemalov, 2012. Study of Disperse Polymer Systems for Producing High-Quality Polymeric-Bituminous Materials. Chemistry and Technology of Fuels and Oils, 48(5): 339-343.

4. Kemalov, A.F., 2003. Effect of Activators in Production of Oxidized Bitumen. Khimiya i Tekhnologiya Topliv i Masel., 1-2: 64-67+i.

5. Kemalov, A.F. and R.A. Kemalov, 2012. Research of a Disperse Condition of Polymeric Systems for the Purpose of Receiving High-Quality Bitumen-Polymeric Materials. Chemistry Technology of Fuels and Oils, 5: 3-7.

6. Kemalov, A.F. and R.A. Kemalov, 2008. Manufacture of the Oxidized Bitumens. Kazan State Technology University Press, pp: 120.

7. Kemalov, A.F., 2003. Effect of Activators in Production of Oxidized Asphalts. Chemistry and Technology of Fuels and Oils, 39(1-2): 76-81.

8. Kemalov, R.A., 2003. The modified special bitumens and paintwork materials on their basis, Cand. Sci. (Tech.) Dissertation, Kazan State Technology University.

9. Kolbanovskaya, A.S. and V.V. Mikhaylov, 1973. Road Bitumens. Transport Publ., pp: 1-264.

10. Kemalov, R.A. and A.F. Kemalov, 2011. Structural the Dynamic Analysis by Means of a Nuclear Magnetic Resonance in Oil and Gas Technologies (Article). Increase in Oil Recovery – the Priority Direction of Production of Stocks of Hydrocarbon Raw Materials. The Fan of AN RT Press, pp: 526-528.

11. Castellanos-Díaz, O., F.F. Schoeggl, H.W. Yarranton and M.A. Satyro, 2013. Measurement of Heavy Oil and Bitumen Vapor Pressure for Fluid Characterization. Industrial and Engineering Chemistry Research, 52(8): 3027-3035.

12. Carrillo, J.A. and L.M. Corredor, 2013. Upgrading of Heavy Crude Oils: Castilla. Fuel Processing Technology, 109: 156-162.

13. Singh, B., L. Kumar, M. Gupta and G.S. Chauhan, 2013. Polymer-Modified Bitumen of Recycled LDPE and Maleated Bitumen. Journal of Applied Polymer Science, 127(1): 67-78.

14. Zhang, H., X. Jia, J. Yu and L. Xue, 2013. Effect of Expanded Vermiculite on Microstructures and Aging Properties of Styrene-Butadiene-Styrene Copolymer Modified Bitumen. Construction and Building Materials, 40: 224-230.

15. Baldino, N., D. Gabriele, F.R. Lupi, C. Oliviero Rossi, P. Caputo and T. Falvo, 2013. Rheological Effects on Bitumen of Polyphosphoric Acid (PPA) Addition. Construction and Building Materials, 40: 397-404.

16. Quintero, L.S. and L.E. Sanabria, 2012. Analysis of Colombian Bitumen Modified with a Nanocomposite.

17. Golzar, K., A. Jalali-Arani and M. Nematollahi, 2012. Statistical Investigation on Physical-Mechanical Properties of Base and Polymer Modified Bitumen Using Artificial Neural Network. Construction and Building Materials, 37: 822-831.

19. Arslan, D., M. Gürü and M.K. Çubuk, 2012. Performance Assessment of Organic-Based Synthetic Calcium and Boric Acid Modified Bitumens. Fuel, 102: 766-772.

20. Mahmoudkhani, A., T. Fenderson, P. Watson, Y. Wu and M. Nair, 2012. New Environmental Friendly Process Aids Improve Bitumen Recovery and Accelerate Tailings Settling of Low Grade Oil Sands. In SPE Hydrocarbon Economics and Evaluation Symposium, pp: 6-13.