



Evaluation of Synthesized Catalytic Complex Structure-Forming Ability during Paraffin Base Tar Upgrade

Alim F. Kemalov¹, Ruslan A. Kemalov*², Adiko Serge-Bertrand³

¹Kazan Federal University

*Corresponding author E-mail: kemalov.ruslan@gmail.com

Abstract

The combination of the synthesized multicomponent bifunctional catalytic complex (MBC) components with heavy oil residues (HOR) of the paraffin-naphthenic (P-N) base leads to the chemical structuring of the hydrocarbon (HC) segments of the raw material molecules, and the specifics of HOR physicochemical structure, which will be the criteria for the selection of modifiers with a certain chemical nature [1,2,3,4]. It has been established that the introduction of catalytic activators in the tar composition promotes both the intensification of the oxidation process and the production of bituminous insulating material (BIM) with high physicomechanical properties [1,2,4].

Raw materials for the production of special bituminous materials must be highly resinous with a P-HC content of up to 3% by weight. Based on the works by A.S. Kolbanovskaya [6], this is explained by the fact that the dispersed structure of bitumen is significantly dependent on the content of P-HC, since the dispersed phase in the oils is formed by naphthenic (N-) and PN-A-HC at certain temperatures with the side chains of the paraffinic P-HC series. If their content is more than 3% by weight the crystallization skeleton of P-HC is developed, which provides stiffness and reduces the plasticity interval for the system. Together with this, it is known that in the process of HOR oxidation the amount of low-molecular-weight oil A-HC decreases continuously, and the relative amount of PN-HC increases. Due to this, the affinity of the dispersion medium (DM) decreases to asphaltenes [7,8,9], which, moreover, becomes larger, which leads to THE deterioration of the cohesion and adhesion-strength properties of BIM.

Keywords: physico-chemical mechanics, heavy oil residual raw materials, paraffin hydrocarbons, catalytic complexes, pulsed NMR spectroscopy, bituminous insulation materials.

1. Introduction

According to the physico-chemical mechanics of petroleum disperse systems (FCM PDS), the correct understanding of the composition and the structure of HOR raw materials makes it possible to solve the problems of qualitative BIM creation scientifically [1,2,7,8]. Raw materials for insulating bitumen obtaining should be highly resinous with a minimum content of PN-HC. In the process of HOR processing, in particular, the tar of the Elkhovsky NPJSC of PJSC Tatneft or the ENPU, the PN-HC base, it becomes necessary to use such chemically active modifiers which would subject the paraffin chain segments to chemical structuring with the subsequent formation of macromolecular polycyclic naphthenic fragments due to an effective intermolecular diffusion [1, 2,4,5,7].

2 Methods

When they considered the possibilities of HOR processing (Table 1) in the activated state, the chemistry of the oxidation process is based on radical chain reactions of oxidative polymerization [1,2,7,10].

The following measurement modes were used for tar analysis: the starting period $T = 500$ msec - 2 s, the interval between 90° and 180° pulses $N = 5 - 1000$, the number of accumulations $n = 3 - 50$ [1,2]. The analysis time did not exceed 3 min.

In the process of HOR, ENPU tar processing (Table 1), it becomes necessary to use such chemically active modifiers which, due to an effective intermolecular diffusion, would subject the segments of paraffin chains to chemical structuring with the subsequent formation of macromolecular polycyclic naphthenic (PN) fragments. The compounds of the naphthene series in the systems under consideration interact better with P-HC rather than with aromatic (A-) hydrocarbons, which in its turn exhibit weak interaction forces with P-HC. On the basis of this approach, HOR structure should acquire a high-resinous type, and during the structures related to the chemical composition of asphaltenes are formed during oxidation, but it has the physicochemical properties of "heavy" resins [10, 11]. Thus, the obtained sample of special bitumen should be characterized by a rather high content of film former - resins with a small amount of P-HC and asphaltenes.

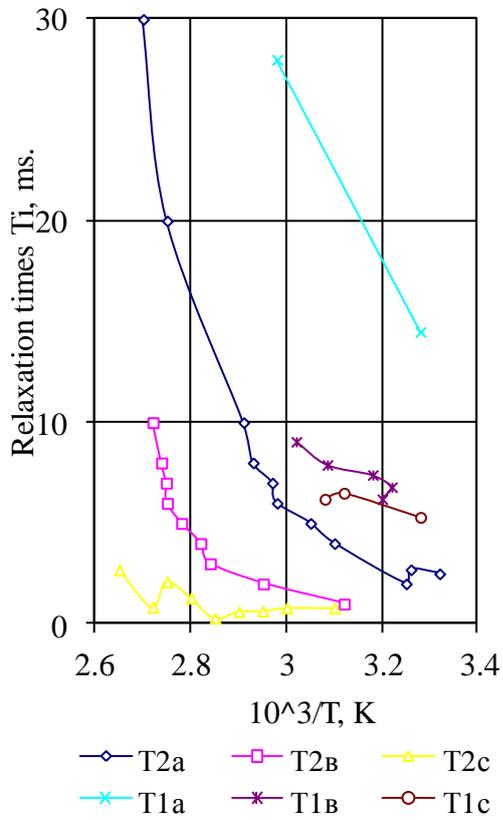
3 Results

Table 1: Physicochemical properties of ENPU tar oil

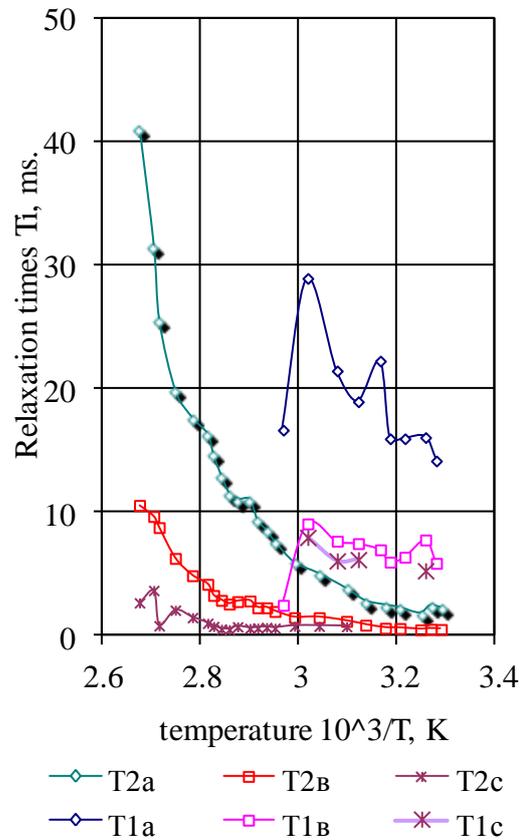
Indicators	Values
density, kg/m ³	0,9878
Assumed viscosity, AV ₈₀	51,76



Content, % weight:	
- SAV	28,23
- sulfur	0,887
- paraffins	15
Asphaltenes/resins	0,45

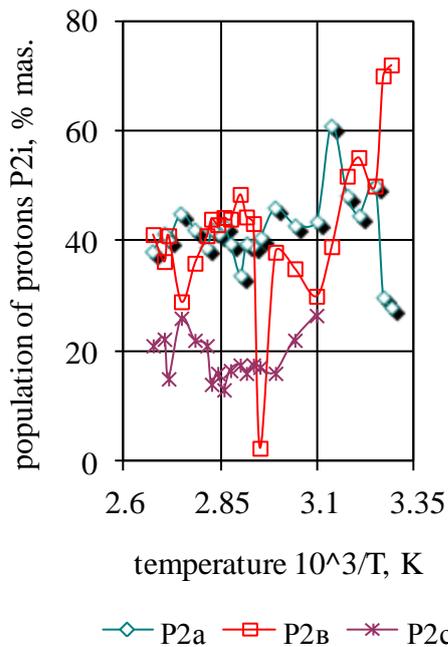


a - oil tar

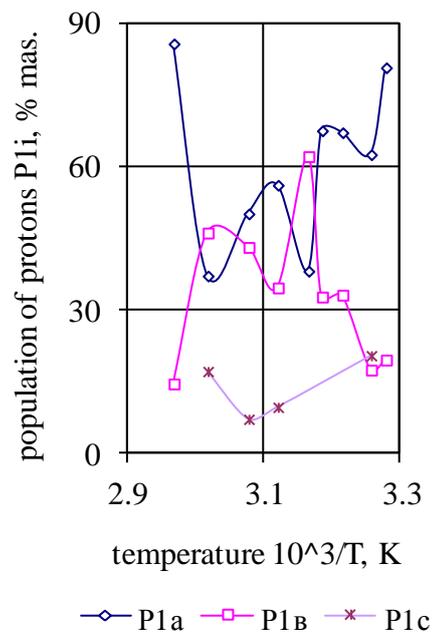


б - oil tar - byproduct

Picture 1: The change in the relaxation times T_i as a function of temperature

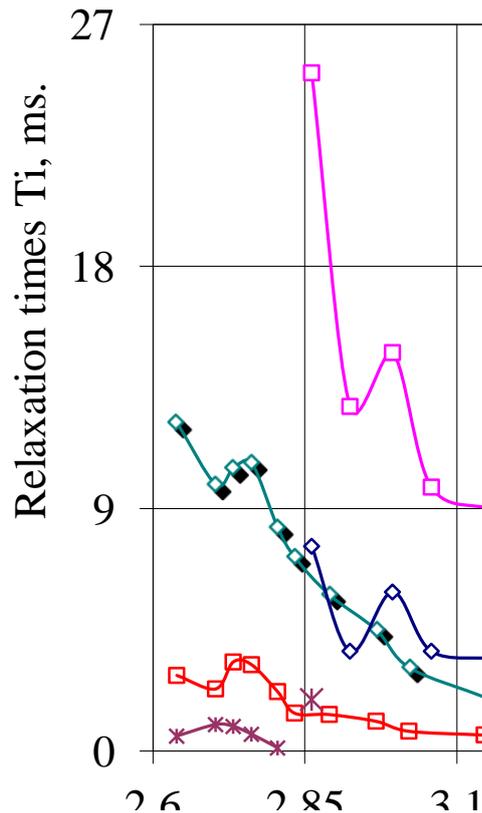


a - spin spin system

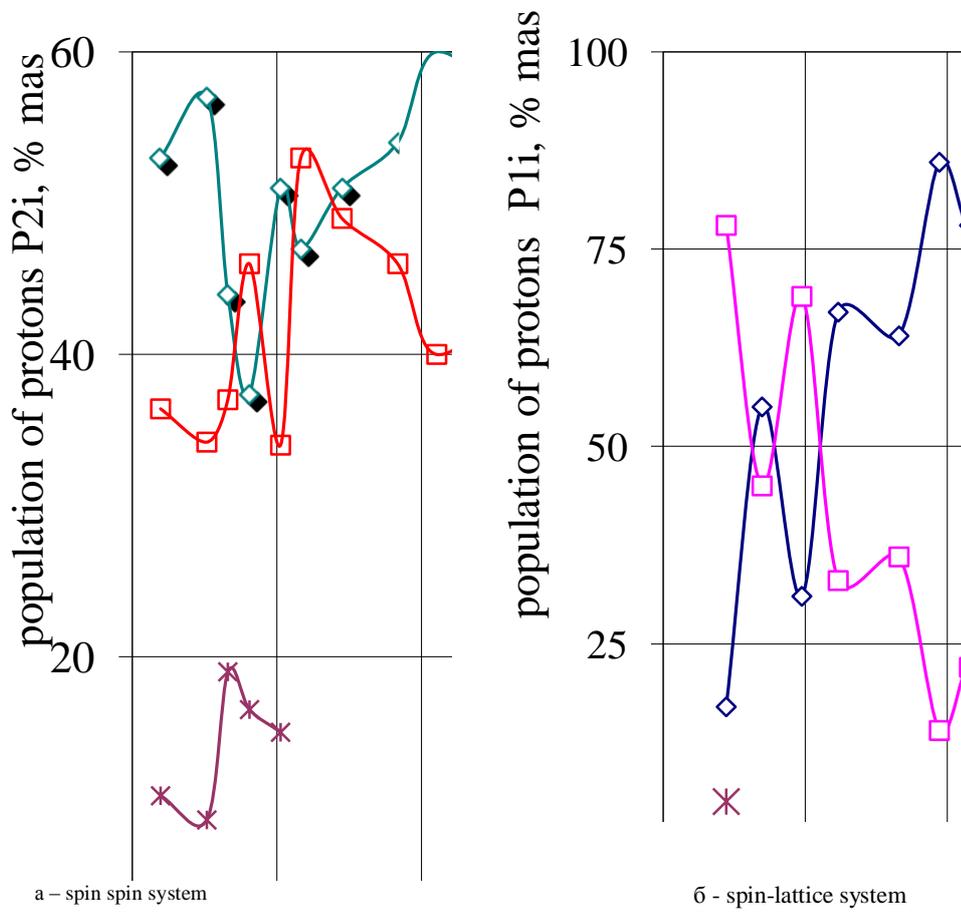


б - spin-lattice system

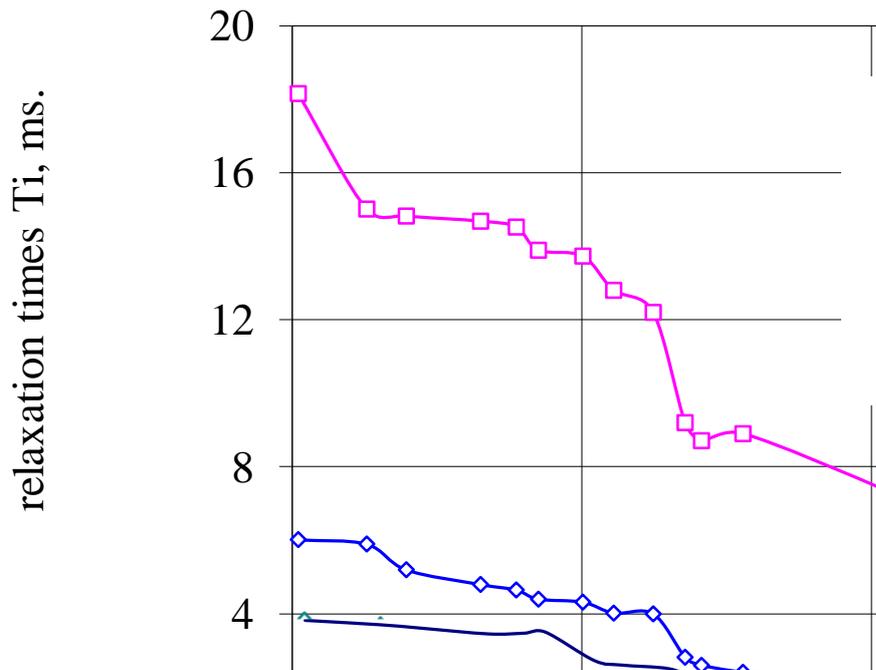
Picture 2: Dependence of the populations of protons of oil tar - byproduct from temperature



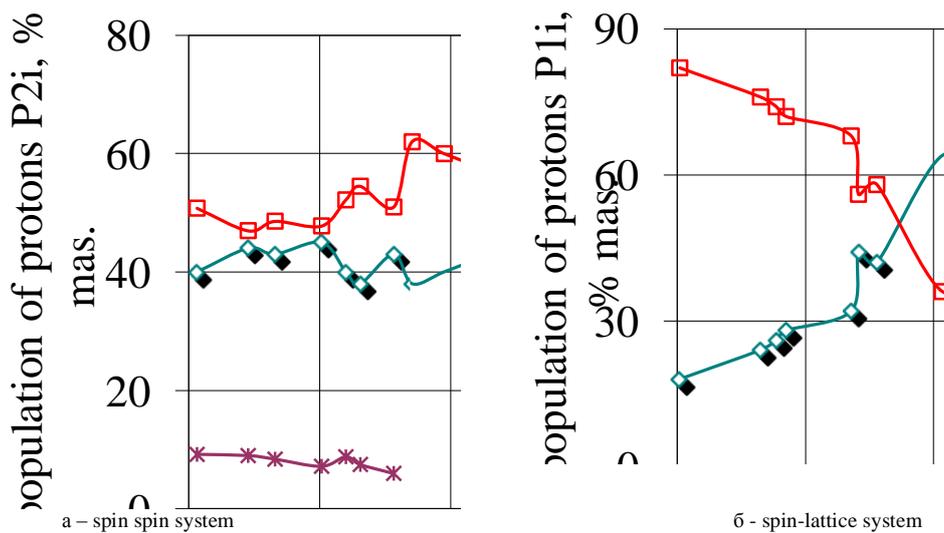
Picture 3: Changing the relaxation times oil tar - byproduct - KPSO depending on temperature



Picture 4: Dependence of the populations of protons of oil tar - byproduct - KPSO from temperature



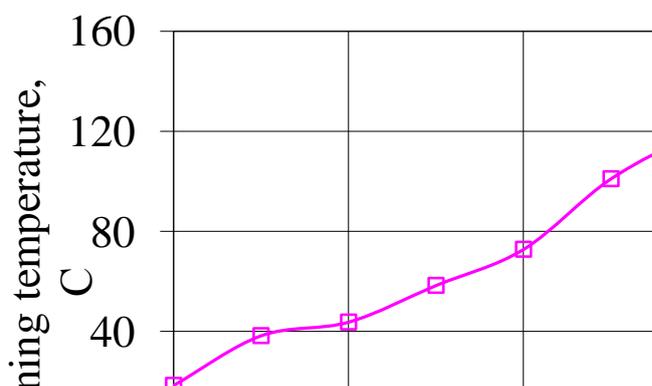
Picture 5: Changing the relaxation times of oil tar - byproduct – KPSO - DM depending on temperature



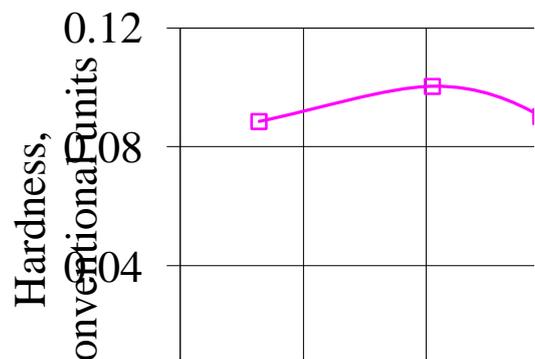
Picture 6: Dependence of the proton populations of oil tar - byproduct – KPSO - DM from temperature

The high degree of HOR structuring is confirmed by the fact that (Fig. 5) at 50°C ($3,096\text{K}$) $> T_{\text{EXP}} > 24^{\circ}\text{C}$ ($3,367\text{K}$) CCE in the structural-dynamic analysis (SDA) is a single phase, then in the interval 89°C ($2,762\text{K}$) $> T_{\text{eksp}} > 50^{\circ}\text{C}$ ($3,096\text{K}$) two phases are

shown - oily and resinous-asphaltene. Small differences in the molecular mobility of phase B and C also determine their high degree of chemical affinity.



Picture 7: Dependence of the softening temperature of bitumen on the duration of oxidation of modified oil tar



Picture 8: Dependence of hardness of BIM on softening temperature

4. Discussion

The regulation of oxidized bitumen properties was carried out in accordance with the main provisions of FCM [1,2,7,8,9,12] by directional regulation of their spatial DS through the change of dispersed phase (DP) particle size by the introduction of MBC into the process of joint oxidation. Bifunctionality (Fig. 7, 8) consists both in HRO oxidation time reduction, and in the necessary improvement of the basic physico-mechanical properties obtained at its BIM. The following components were used as MBK components: the byproduct process component, the synthetic oil production component (KPSO) and the metallized DM complex.

It was established that the byproduct provides a light oxidizability for coatings, since it contains the components actively interacting with air oxygen, namely unsaturated acids, mixed with rosin acids. To ensure that both the total ether and the acid were involved in the subsequent film formation of the bitumen solution in various media, KPSO and byproduct were introduced into the tar with an intensive stirring and the temperatures up to 180 °C, since it is known that unsaturated acids are not able to form a solid film as the result of oxidative polymerization. The violation of the technological process of component combination (temperature increase) or a change of additive introduction stages led both to the course of DM reaction decomposition, and to the deterioration of the physico-mechanical properties of BIM in the future. The acknowledgment of the theoretical prerequisites for the chemical activity of MBC was the study of the structural-dynamic states of HOR of paraffin base by the NMR method when it was combined with MBC components [1,2,13,14,15].

During the analysis of Fig. 1, it should be noted that for the compared systems tar and by-product phase A and C are detected at the same T_{exp} . So for tar at $T_{exp} = 31.87$ °C, the spin-spin relaxation time T_{2A} is 2.5 ms, and for the tar-byproduct system at $T_{exp} = 31$ °C T_{2A} is 2.26 ms. The detection of phase C for tar systems and tar-byproduct occurs at T_{exp} 49.58 and 50 °C with spin-spin relaxation times T_{2C} of 0.8 and 0.77 ms, respectively.

The presence of T_{2S} minimum 0.3 ms at 2.85 K for tar is explained by the conformational difficulties of the spatial arrangements of paraffin-naphthenic chains in the molecules of asphaltenes. In the future, with the growth of T_{exp} , the values of the relaxation times T_{2A} and T_{2C} for the considered SDS are completely convergent.

The studies of T_{2B} dependences on T_{exp} (Fig. 1) show that phases B are detected for the following systems: tar at 47.51 °C, tar-byproduct at 31 °C, where T_{2B} makes 1 and 0.54 ms. At the same time tar-byproduct shows a slight increase of T_{2B} at $T_{exp} \geq 90$ °C. The analysis of the thermodynamic features of spin-lattice changes with the increase of T_{exp} (Fig. 1b) shows the presence of characteristic extrema for T_{1A} and T_{1B} , which can be expressed by steric hindrance during the segmental mobility of the newly formed system. At that it should be noted that the introduction of byproduct into tar does not fundamentally affect the thermodynamic stability of the SDS as a whole, since the relaxation times $T_{1A,B,C}$ for the HOR under study are in the same range of values.

Taking into account the fact that during the thermal treatment at $T = 250-280$ °C the polymerization inhibitors break down and the transition of isolated double bonds in the acyl residues to the more active conjugate state occurs, it should be noted that analogous chemical transformations occur in byproduct, but with slightly lower reaction rates. This is explained by the fact that byproduct refers to the group of saturated film-forming systems ($ICH_{PPD} = 4,3664$). The reaction of isomerization during heat treatment is based, first of all, on partial transitions of isolated double bonds into a more active state, respectively, and the structuring of HOR with the introduction of byproduct occurs insignificantly. However, byproduct use is advantageous by the fact that at low isomerization rates, low polymerization rates are observed during the thermophysical alignment with HOR. This fact, in its turn,

plays an important role in the storage of HOR, since in this case there will be no sharp increase of acid numbers (AN), viscosity, specific weight with a simultaneous IN decrease, which will subsequently deactivate MDC for HOR.

The pronounced ordering of HOR chemical structure, which is the system of tar-byproduct, is observed when it is combined with KPSO (Fig. 1b, 2-4).

According to the comparative analysis of the structural-dynamic parameters of Fig. 1-4 it follows that the branched structure of the KPSO molecule has a structuring effect aimed at the isomerization of PN-HC structure of the most mobile phases A and B. This is confirmed by the data (Fig. 3, 4a) of the spin-spin relaxation $T_{2A,B}$ and $P_{2A,B}$, where the decrease of $T_{2A,B}$ values and the increase of protons $P_{2A,B}$ populations are observed as compared with the values for tar - byproduct (Fig. 1b). The study of the experimental data characterizing the change of proton P_{2i} populations with T_{exp} (Fig. 4a) increase the tar-byproduct - KPSO shows the symbiosis of P_{2B} and P_{2C} and the antipate nature of P_{2A} values from $P_{2B,C}$. This is explained by the fact that the macromolecular mobility of the terminal groups of the structured phase A increases to a certain P_{2A} limit with the growth of T_{exp} , and then, as the result of their proximity to the segmental part of the kinetic chains of phase B, the T_{2B} precession frequency increases (Fig. 3) and, thus, the growth of P_{2B} is observed (Fig. 4a).

Due to the affinity of chemical structures of byproduct and tar maltens, interfacial diffusion of the components takes place. We believe that when KPSO is combined with HOR PN-HC base at 80-100 °C, the physico-chemical structure is already changing by macromolecular isomerism of P-HC structures into polycyclic naphthenic ones with a high degree of the carbon chain isostericity, i.e. by the content of methyl and ethyl end groups. The presence of C = C double bonds in the composition of byproduct is apparently expressed by the extremes of T_{2i} and P_{2i} values, which show their activity at T_{exp} above 80 °C, since they are in the newly formed PCN-HC structures. At the same time, the contained double bonds in byproduct pass into the PCN-HC structures, which are within some limits of T_{exp} to P_{2B} or to P_{2C} during P_{2i} measurement. Subsequently, during the oxidizing of HOR, we believe, they are transformed without any special difficulties into the PCN-A-HC of the asphaltene system, or remain in the original state, initiating a spin-lattice system to create related resinous structures. The last type of chemical structuring is most acceptable, because localized C = C double bonds in H-HC structures are affected to spatial structuring only in the case of intense oxidation, which is ensured only after the application and the evaporation of solvent and the shrinkage of BIM on the substrate, where it proceeds at high velocities due to the small thickness of BIM (30-50 μ m) and the maximum contact of a small BIM area with air oxygen. This statement is based on the fact that liquid-phase high-temperature oxidation causes an incomplete use of oxygen supplied to the reactor (up to 50% by weight), and, thus, thermal destruction over structuring predominates in the process. These assumptions are confirmed by high physicochemical properties of BIM, associated with a high degree of film-forming material oxidation, the result of which are newly formed (at the physical mixing of KPSO with tar-byproduct) NA-HC structures and C = C double bonds of byproduct.

The comparative analysis of the thermodynamic states of the spin-lattice systems of tar-byproduct and tar-byproduct - KPSO (Fig. 1b, 2-4) shows that the introduction of KPSO enhances the structuring effect of byproduct, with the same extreme structural-dynamic states at identical T_{EXP} , but even at smaller T_{1i} .

Fig. 2b and 4b show that due to the symbiosis of the phases B and C, the chemical inhomogeneity of the maltens is observed. Due to the fact that some part of HOR system, mainly the phases A and B, as well as alkyl substituents of phase C, tend to ordering, i.e. to the creation of PCN-HC structures, then for TDO, expressed by the increase of P_{1B} , the PCN-HC and the isomers of P-HC

structures are responsible that predominate in the maltens of the newly formed system. Thus, from Fig. 3 and 4 it can be seen that in the temperature range of $83.5\text{ }^{\circ}\text{C}$ (2.805 K) $> T_{\text{exp}} > 45\text{ }^{\circ}\text{C}$ ($3,145\text{ K}$) there is a single resinous-asphaltene phase $P_{2B} = 44.4\text{--}53\%$, i.e. the sum of the phases B and C; and at T_{exp} above $83.5\text{ }^{\circ}\text{C}$ the phase C is manifested, at that the quantitative content of phase B decreases, and the quantitative content of phase A increases, i.e. $P_{2A} = 51\%$, $P_{2B} = 34\%$, $P_{2C} = 15\%$. In this regard, the generalization of the most mobile phases A and B - "maltenes" in NMR relaxometry does not agree with the ongoing studies of HOR chemical structure. Since at initial or final T_{EXP} the phase C falls out from the structural-dynamic analysis of HOR, due to the chemical affinity and molecular mobility of resin and asphaltene components, and when the phase C response takes place, the characteristic decrease in P_{2B} is observed, so the generalization must be made between the phases B and C - resinous-asphaltene phase.

The reaction of macromolecular structuring of byproduct, KPSO and tar components introduced into HOR composition of the catalyst leads to the newly formed SDS and CCE, respectively, to the state of thermodynamic equilibrium, which is expressed by the decrease of the spin SDS system relaxation times of SDS in comparison with the previously studied HOR with the participation of tar and stepwise introduced modifiers (Fig. 1, 3, 5).

An important distinctive feature of the studied HOR is the disappearance of the spin-lattice relaxation times of T_{1C} (Fig. 5) and, accordingly, the population of P_{1C} protons (Fig. 6b). This is explained by the initiation of deep interphase structuring reactions, directed, in our opinion, to the isomerization of long-chain P-HC fragments in maltenes and substituted aliphatic chains in asphaltenes with a small degree of branching.

5 Conclusions

It is determined that during the introduction of byproduct into tar, the structuring of the most mobile phases A and B takes place, expressed by the decrease of their segmental mobility, that is:

a) due to an insignificant decrease of T_{2A} at $68\text{ (}2.933\text{)} > T_{\text{exp}} > 31\text{ }^{\circ}\text{C}$ ($3,289\text{K}$). At $T_{\text{exp}} > 68\text{ }^{\circ}\text{C}$ in tar - byproduct T_{2A} 8 ms. is less than T_{2A} 8.5 ms. for tar, which is obviously associated with steric hindrance of the molecular mobility of alkyl segments in paraffin-naphthenic structures;

b) due to the mutual diffusion and the affinity of byproduct and tar components, minor differences are observed during proton relaxation T_{2B} , where the values of T_{2B} for tar are to a lesser degree exceed those for tar - byproduct, which reflects the ordering of HOR chemical structure.

At the stage of physical combination of byproduct and tar at $80\text{--}100\text{ }^{\circ}\text{C}$, the initial stage of the polymerization reaction takes place (with an insignificant access of atmospheric oxygen), which subsequently proceeds with the thermo-oxidative degradation of HOR and ends on the substrate directly.

6. Summary

Ultimately, based on small values of the spin system molecular mobility (Fig. 5), with a simultaneous absence of extrema $T_{2A,B}$ and the disappearance of the phase C of the spin-lattice system T_{1C} with T_{exp} increase, it can be concluded that the predominant fragmentary structure of the newly formed system tar - byproduct - KPSO - DM is a naphthenic with a developed substitution system by alkyl chains, which is proved (Fig. 6) by the presence of extremes P_{2A} and P_{2B} . Thus, (Fig. 7, 8) the introduction of activators into the composition of tar makes it possible to intensify the oxidation process and to obtain BIM with high physical and mechanical properties.

Acknowledgements

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

References

- [1] Kemalov A.F. Intensification of oxidized bitumen production and modified bituminous materials based on their basis. - Diss. by Doctor of Technical Sciences. Kazan: KSTU, 2005. 354p.
- [2] Kemalov A.F. Structural and dynamic studies of adsorption-active coagulation structures of bulk nanocrystalline materials in petroleum disperse systems / Kemalov A.F., Kemalov R.A. The Grant from the Ministry of Education and Science of Russian Federation, KSTU. Entrance number И110120123609. FGNU "Center for Information Technologies and Executive Authority Systems of R&D №26 /1-2-1-14-ONTI issued on 27.01.2011, reg. number 01201152519 01.01.2011 - 31-12-2015.
- [3] 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.
- [4] Bayasgalan H. Chemical modification of highly paraffinic oil residues in raw materials for bitumen production (using the example of Mongolian oils): dis. for the degree of Chem. Science Candidate: 02.00.13 / Hulan Bayasgalan. - Tomsk, 2008. - 98 p.
- [5] Badamdorzh. Davaatsaren. The changes in the composition and the properties of highly paraffinic oils in the processes of unconventional influence (on the example of Mongolia oils): the author's abstract from the dis. of tech. science cand. Tomsk Polytechnic University, Tomsk, 2008.
- [6] A.V. Kolbanovskaya. Road bitumen. / A.S. Kolbanovskaya, V.V. Mikhailov - Moscow: Transport, 1973. - 264 p.
- [7] Kemalov, A.F. and R.A. Kemalov, 2013. 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*, 23 (1): 51-55.
- [8] Kemalov A.F. The study of the disperse state of polymer systems for the purpose of high-quality bitumen-polymer material obtaining / Kemalov A.F., Kemalov R.A. // *Chemistry of fuels and oils*. 2012. - №5. pp. 3-7.
- [9] Unger F.G., Andreeva L.N. The paramagnetism of SDS and the nature of asphaltenes. -M., 1986. - 29 p. - (Preprint of the Siberian Branch of the USSR Academy of Sciences).
- [10] Castellanos-DHaz, O., F.F. Schoeggel, 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.
- [11] Carrillo, J.A. and L.M. Corredor, 2013. Upgrading of Heavy Crude Oils: Castilla. *Fuel Processing Technology*, 109: 156-162.
- [12] Sunyaev Z.I. Oil dispersed systems. / Z.I. Syunyaev, R.Z. Syunyaev, R.Z. Safieva - M.: Chemistry, 1990. -226 p.
- [13] Vashman A.A., Pronin I.S. Nuclear magnetic relaxation and its application in chemical physics. Moscow: Nauka, 1979, 236 p.
- [14] 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.
- [15] 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.