

Article

Use of Lignite Processing Products as Additives to Road Petroleum Bitumen

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Abstract: It is known that there are significant deposits of lignite (brown coal) in Ukraine, particularly in categories A + B + C1. At the same time, certain technical and legal obstacles limit its use as an energy carrier. Therefore, new methods of using lignite and processing its products are necessary. The latter includes humic acids. It was suggested that these acids could be used to stop road bitumens from breaking down. This is because they are antioxidants that contain functional phenolic and carboxyl groups. In particular, this article analyses the nature of the influence of humic acids on the physical and mechanical properties of road petroleum bitumen and its resistance to technological aging. It was found that at a modification temperature of 120 °C (duration-60 min., consumption of humic acids-2.0 wt.%), this additive has a slight negative effect (changes are within permissible limits) on the plastic properties of bitumen and slightly improves its elasticity. The main reason for adding humic acids to road bitumen under the specified conditions is to improve its resistance to technological aging compared to the original binder.

Keywords: lignite; humic substances; humic acid; road bitumen; modification



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1. Introduction

As commonly known, in addition to being combusted in thermal power plants, lignite (brown coal) is part of the raw material base of many technological processes, particularly gasification and oxidative desulfurization, and it is also used as a raw material for obtaining components of boiler fuel or bitumen [1–4]. For example, the authors of [5] provide complex study results on using lignite from the Oleksandriysk deposit of Ukraine for combined gasification with the coal tar of coke chemical origin and walnut shell. The authors of [6,7] present the prospects and economic feasibility of the developed gasification method using low-temperature plasma.

The use of lignite in known methods and the development of new ones is relevant because of its significant resources. For example, in Ukraine, the largest lignite deposits of category A + B + C1 are located in the Dnipropetrovsk (1,320,644 thousand tons), Kirovohrad (750,833 thousand tons), and Kharkiv (389,985 thousand tons) regions. The average annual amount of lignite in this category, mined in Ukraine, is 9331 thousand tons [5].

On the other hand, regardless of the amount of mined lignite, it is used in a limited amount in energy and other industries based on the negative features of its quality characteristics, such as the high content of sulfur, ash, and moisture [1]. In addition to technical obstacles, the legal problems of using lignite resources often arise. For example, the “Energy Strategy of Ukraine” will operate in Ukraine until 2050, the main goals of which are to

achieve the maximum level of climate neutrality and maximum reduction in the use of lignite, and to increase the efficiency of resource use, including the creation of new products and innovative solutions in the energy sector [8].

Given the above, it can be stated that the search and development of non-energy-related utilization paths for lignite is a very promising scientific and practical task.

One of the valuable products of processed lignite is humic acids. This type of substance is a natural organic compound formed in the process of humification—the microbiological transformation of plant, animal, and microbial origin products, which occurs in a moist soil environment with insufficient access to oxygen. Their main part is resistant to biochemical decomposition and accumulates in soil, biohumus, sapropel, peat, and lignite. From the latter, humic acids can be extracted using alkali solutions in the salt-form humates [9,10]. This method is based on the industrial method of obtaining humic acids. At the same time, according to the research, humic acids can also be produced by fermentation using palm fiber waste as a substrate (the empty fruit bunch (EFB) of palm trees as a substrate) [11] and via chemical synthesis using condensation and polymerization reactions [12,13].

Humic acids extracted from different sources of raw materials differ in their compositions and ratios of the main groups of substances; however, they remain unchanged, particularly the following substances:

- Fulvic acids, which are soluble in water;
- Hematomelanic acids, which are insoluble in water but soluble in alcohol;
- Humic acids, which are insoluble in neither water nor alcohol.

The source variety of the raw materials also leads to different concentrations of humic acids ranging from 10 to 96 wt.% in the finished product [14]. Humic acids contain different functional groups, whose numbers depend on the origin, age, climate, and environmental conditions of acid extraction/production [15]. However, for the most part, the properties of humic acids are directly related to the presence of oxygen-containing groups in their composition, primarily phenolic and carboxylic [16].

All of the above involve a wide range of uses of humic acids and salts. For example, potassium/sodium humate is a widespread activator of plant growth, which is actively used in agriculture to improve its resistance to environmental factors [9]. Humic acids are used as a structuring agent in polymer hydrogels based on gelatin [1], as well as in the creation of sorbents for groundwater purification, particularly from copper and cadmium ions [7,17] or for the removal of aflatoxins from edible oils [18]. Because they are made up of functional groups and quinones, these acids also have anti-oxidant, dismutagenic, and fungicidal properties [13].

They can also fight viruses and reduce inflammation. At the same time, due to the antioxidant properties of humic acids, they can be used to slow down the aging processes of petroleum binders, particularly road bitumen.

The aging of bitumen is divided into two stages: technological and operational. In the technological stage, during the preparation, transportation, or laying of the asphalt concrete sheet, the percentage of loss of binding properties is much higher than that in the operational stage. These processes are known to actively occur under the influence of high temperatures, moisture, and solar radiation during the contact of hot bitumen with atmospheric oxygen in the production stage, pumping of hot road bitumen through gutters, and storage of the finished binder in tanks with a large area of contact with air, as well as during the subsequent production of ready-made hot asphalt mix.

As a result, the bitumen structure undergoes significant changes, becoming hard and brittle due to the increase in the number of asphaltenes and the decrease in the number of oil components. During further operation of the road surface, the described defects only accumulate, significantly reducing the period between repairs.

To slow down the bitumen's loss of its binding properties as an antioxidant, the authors [14] used potassium humate with different concentrations of humic acids (from 30% to 85% by weight, depending on the raw material). According to research, samples of modified bitumen with the addition of 3% humic acid salt at a concentration of 85% by

mass to oxidized bitumen and with the addition of 1 wt.% demonstrate the best resistance to technological aging. of the same salt to residual bitumen. Thus, it can be stated that humic acid salts are quite promising antioxidants for the technological aging of bitumen.

The latest research is especially relevant for countries with clearly expressed changes in climatic phenomena by season, particularly for Ukraine, given that sharp changes in environmental temperatures and a significant amount of precipitation during the year directly affect the road surface condition and service life [14].

Studies related to the interaction of humic products obtained during the processing of lignite with bitumen look especially interesting and promising due to a certain similarity in the structure of bitumen molecules and humic acids (Figures 1 and 2). This is primarily due to the presence of condensed cyclic aromatic compounds in their structure. Given the above, it can be assumed that bitumen and humic acids are compatible substances. At the same time, the presence of oxygen-containing groups in humic acids can become an additional connecting link for their interaction.

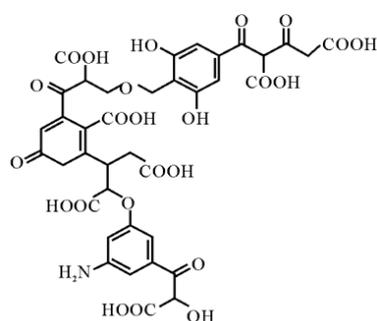


Figure 1. Two-dimensional planar molecular structure model of humic acid [19].

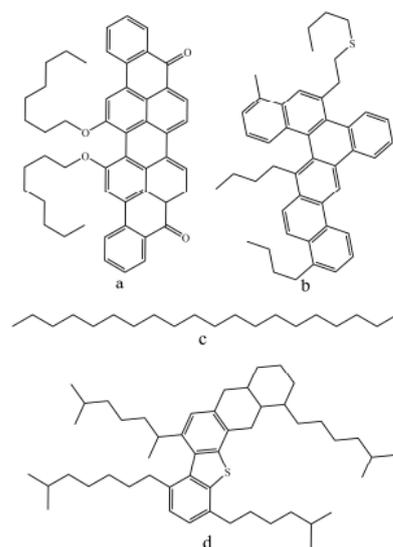


Figure 2. Molecular structures of bitumen component (SARA) fractions: (a) asphaltenes ($C_{50}H_{48}O_4$), (b) aromatics ($C_{46}H_{50}S$), (c) saturates ($C_{20}H_{42}$), and (d) resins ($C_{50}H_{80}S$) [20].

Based on the above, it was decided to investigate the nature of the influence of humic acids on the quality characteristics of road bitumen.

To achieve this goal, it is necessary to perform the following tasks: take lignite from Ukraine, analyze it, extract humic acids from it and make their comprehensive analysis; investigate the effect of adding humic acids to road bitumen quality indicators.

2. Materials and Methods

2.1. Materials

Humic acids were extracted from an averaged sample of lignite of Ukrainian origin (Cherkasy region). Characteristics of lignite according to indicators of technical and elemental analyses and values of higher and lower heating value are given in Tables 1 and 2. The chemical analysis of lignite ash is provided in Table 3.

Table 1. Technological properties of lignite *.

Proximate Analysis of Lignite, wt. %					Heat of Combustion, MJ/kg	
W_t^r	W^a	A^d	S_t^d	V^d	Q_s^{daf}	Q_i^r
17.0	16.8	48.7	2.50	29.1	33.88	13.60

* W_t^r —moisture in working condition, %; W^a —moisture in analytical condition, %; A^d —ash on dry condition, %; S_t^d —dry sulfur content, %; V^d —volatile matter in the dry condition, %; Q_s^{daf} —the highest heat of combustion in dry ashless condition, MJ/kg; Q_i^r —lower heat of combustion in operating condition, MJ/kg.

Table 2. Ultimate analysis of lignite *, wt. %.

C^d	H^d	N^d	O_d^d
41.47	2.30	0.66	4.36

* C^d —content of carbon in the dry condition, %; H^d —content of hydrogen in the dry condition, %; N^d —content of nitrogen in the dry condition, %; O_d^d —content of oxygen in the dry condition, %.

Table 3. Chemical composition of lignite ash *, wt. %.

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	SO_3
70.08	9.83	3.24	0.88	5.43	0.77	0.90	5.90

* SiO_2 —content of silicon oxide, %; Al_2O_3 —content of aluminium oxide, %; Fe_2O_3 —content of iron oxide, %; MgO —content of magnesium oxide, %; CaO —content of calcium oxide, %; Na_2O —content of sodium oxide, %; K_2O —content of potassium oxide, %; SO_3 —content of sulfur oxide, %.

The characteristics of humic acids obtained from lignite, namely the technical and elemental analysis indicators, are given in Tables 4 and 5.

Table 4. Proximate analysis of humic acids *, wt. %.

W^a	A^d	S_t^d	V^{daf}
9.6	7.9	3.90	52.3

* W^a —moisture in analytical condition, %; A^d —ash on dry condition, %; S_t^d —dry sulfur content, %; V^{daf} —volatile matter in the dry ashless condition, %.

Table 5. Ultimate analysis of humic acids *, %.

C^{daf}	H^{daf}	N^{daf}	O_d^{daf}
62.34	4.63	0.77	28.36

* C^{daf} —content of carbon in the dry ashless condition, %; H^{daf} —content of hydrogen in the dry ashless condition, %; N^{daf} —content of nitrogen in the dry ashless condition, %; O_d^{daf} —content of oxygen in the dry ashless condition, %.

The modification with the obtained humic acids was made with oxidized petroleum bitumen of BND 70/100 grade obtained from PJSC Ukrtatnafta (Kremenchuk, Ukraine). Characteristics of oxidized bitumens are given in Table 6.

Table 6. Physical and mechanical characteristics of BND 70/100 bitumen.

Index	Unit of Measurement	Value
Penetration at 25 °C, (P25)	mm	7.8
Softening point, (SP)	°C	52.8
Ductility at 25 °C, (D25)	cm	58
Elastic recovery at 25 °C, (E25)	%	17.5
Adhesion to gravel	mark	3.5
Adhesion to glass	%	65
Resistance to hardening at 163 °C (RTFOT method):		
mass change, (Δm)	wt. %	0.086
softening point (SP) after RTFOT	°C	59.6
penetration at 25 °C (P25) after RTFOT	mm	3.9
softening point change, (ΔSP)	°C	6.8
retained penetration	%	50.0

2.2. Experimental Procedure

Lignite samples, main indicators determination, and humic acids extraction with their further analysis were done at the National Technical University “Kharkiv Polytechnic Institute”. At Lviv Polytechnic National University, humic acids were used to change bitumen samples, and standard methods were used to analyze both the original and changed bitumen samples.

2.2.1. Extraction of Humic Acids from Lignite

The process of synthesis humic acids out of lignite [21] includes grinding the lignite, humic substances extraction with sodium hydroxide solution, the obtained solution neutralization by acid with precipitation of the alkali-soluble fraction (humic acids), filtering, and drying.

Lignite with a particle size of 200 μm was used for alkaline extraction of humic acids. The temperature of extraction of humic acids from lignite is 20–25 °C. For this, 1.0 kg of lignite was treated with 0.8 m³ of 0.1N sodium hydroxide. The obtained suspension was kept for 24 h. Then, decantation was carried out with further processing in a centrifuge at a rotation speed of 2000 rpm. The alkaline solution was separated from the lignite solid particles, and humic acids were precipitated via addition of sulfuric acid to show signs of coagulation (pH = 2). The resulting solution was processed using a centrifuge. The sediment was transferred to a funnel with filter paper and washed with distilled water to pH = 7. The resulting sediment was dried and ground in a porcelain mortar.

This sequence of operations was performed twice to obtain humic acids of high purity.

2.2.2. Preparation of Modified Binders

Modification of road bitumen with humic acids was done under the following conditions:

- Amount of modifier (humic acids)–2.0 wt.%;
- Process temperature–120 °C; 150 °C; 180 °C;
- Duration of mixing–60 min.;
- Rotation speed–1000 min^{−1}.

The modification temperature was changing based on the characteristics of the raw materials and certain technological aspects. Thus, based on the data given in Table 4, it can be stated that the obtained humic acids contain a significant amount of volatile substances (52.3%), which are products of organic nature. Through the data in Table 5,

it can be summarized that the main element of humic acids, (except carbon), is oxygen. Namely, the data in Tables 4 and 5 confirm the presence of a significant number of aromatic compounds with oxygen-containing functional groups in the acids' composition. The ability of the described to undergo chemical transformations depends on the created conditions, including the temperature. Therefore, the temperature of the modification process was a variable parameter. Temperature lower limit (120 °C) depends on the bituminous binder viscosity and mobility, while the upper limit depends on the technological aging of process intensity and the bitumen losing its binding properties at higher temperatures. In addition, the indicated upper temperature limit of the modification process (180 °C) is optimal for many polymer modifiers that are used in industry, particularly for latexes, thermopolymers and thermoplastics.

The duration of the modification process and the amount of the used modifier were determined on the basis of conducted research via usage of humic acid salts as additives to bitumen and taking into account the recommendations of manufacturers of industrial modifiers [22–25].

Modification of bitumen was carried out in a metal container placed on a laboratory hotplate and equipped with a mechanical stirrer and a thermometer. A certain amount of bitumen BND 70/100 was laid into a metal container and heated up to the appropriate temperature. After reaching the indicated temperature and with constant mixing of the sample, the humic acids as a modifier were gradually added in the appropriate amount of 2.0 wt.%. Stirring was maintained at a fixed rotation speed for 60 min to ensure uniform dispersion of humic acids in the bitumen binder.

2.3. Methods of Analysis

The determination of the heat of combustion of lignite was made in accordance with [26]. The main physical and mechanical properties of the original and modified bitumen were determined according to standardized methods. The following were determined characteristics, such as: penetration at 25 °C (P25) [27]; softening point (SP) [28]; elastic recovery at 25 °C (E25) [29]; and ductility (D25) were studied according to the methods described in the works [30,31]. Adhesion to the surface of the glass was assessed according to the Ukrainian standard test methods DSTU 9169:2021 [32], while adhesion to the gravel surface according to the DSTU 8787:2018 [33] The RTFOT method [34] was used for study the resistance of bitumen to technological aging.

3. Results and Discussion

To study more about the structure of humic acid-modified bitumen (HAMB) so that road construction materials can be made, three samples were made, each with a different softening temperature: HAMB-1 at 120 °C, HAMB-2 at 150 °C, and HAMB-3 at 180 °C. The main physical and mechanical properties of BND 70/100 and HAMB are shown in Figure 3.

The results, presented in Figure 3, show that with an increase in the modification temperature from 120 °C to 180 °C, a decrease in the P25 from 7.2 to 5.4 mm is observed, which indicates an increase in the stiffness of the modified samples. There is also a sharp decrease in with the introduction of humic acids from 58.0 cm for unmodified bitumen to 9.5 cm for bitumen modified with 2.0 wt.% at a temperature of 180 °C. At the same time, the introduction of humic acids increases the SP of the modified samples, which gradually increases from 52.8 °C for the unmodified sample to 55.4 °C for HAMB-3. A positive effect is also observed with an increase in E25, which is 28.7% for the HAMB-1 sample, compared to 17.5% for BND 70/100. Adhesion indicators to glass and crushed stone do not change significantly when the modifier is added, and the effect of modification via an increase in temperature is also insignificant.

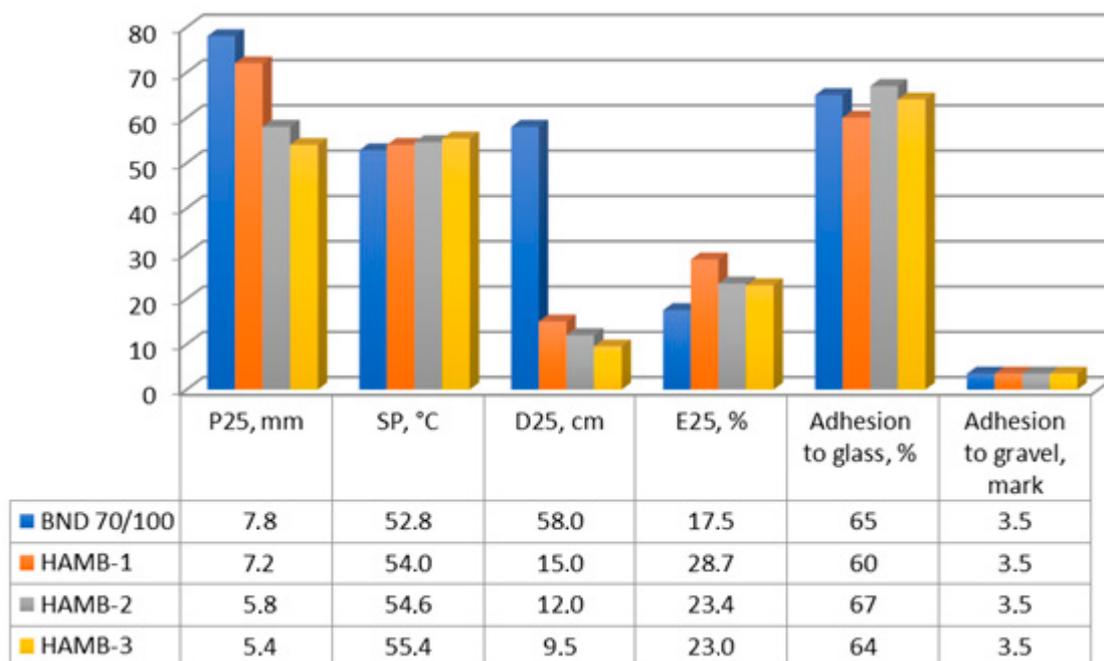


Figure 3. Physical and mechanical properties of BND 70/100 and HAMB.

Thus, as a result of the road bitumen modification with humic acids, at the increases of process temperature, the heat resistance increases and the elastic properties of the bitumen samples improve somewhat at the same time, the plasticity decreases and the hardness increases, i.e., the bitumen partially loses its binding properties.

The resistance to hardening of modified samples is characteristic that allows a comprehensive characterization of the humic acids' influence on the bitumen properties, determined at a temperature of 163 °C using the RTFOT method. The corresponding results are shown in Figure 4.

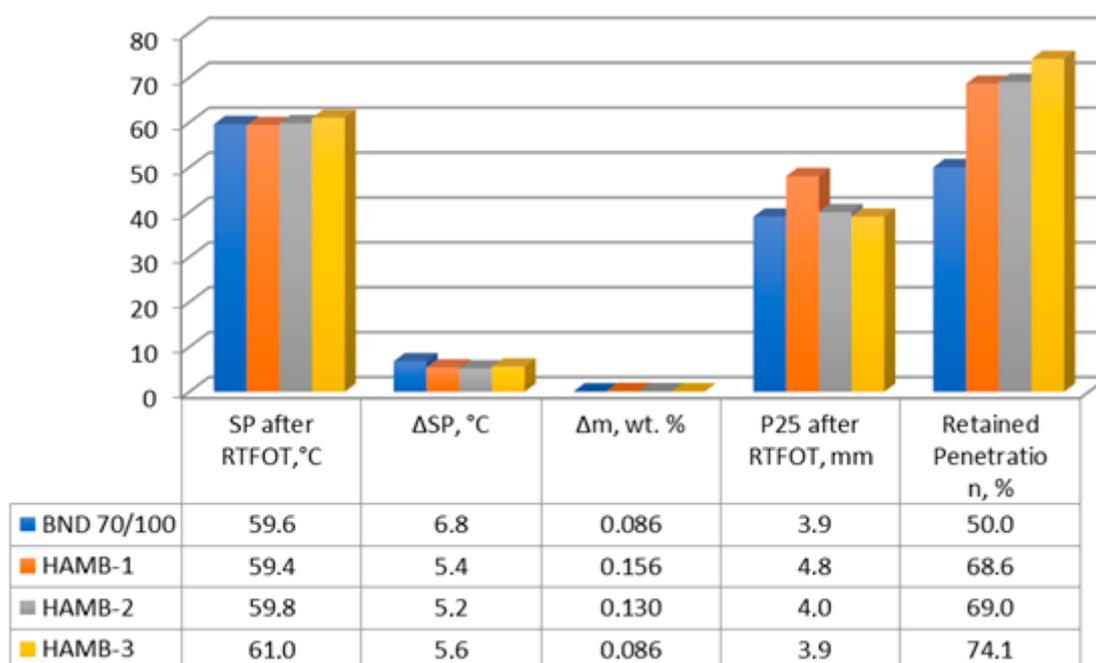


Figure 4. Physical and mechanical properties of BND 70/100 and HAMB after RTFOT aging.

From the given results, it is clear that the addition of 2.0 wt.% of humic acids has a positive effect on increasing the resistance to aging of all samples modified at different temperatures. In particular, there is a slowdown in SP growth in the range from HAMB-3 to HAMB-1. Thus, for the sample HAMB-1, which is modified at 120 °C, SP after RTFOT increases by 5.4 °C, while for HAMB-3 (modified at 180 °C), SP after RTFOT increases by 5.6 °C. These indicators are lower than the SP value of the original bitumen, for which ΔSP is 6.8 °C, so it can be argued that the modified samples have a higher heat resistance than the original bitumen.

The weight loss of the samples increases slightly, and there is also a significant increase in the residual penetration, which increases as the modification temperature rises from 68.6% for HAMB-1 to 74.1% for HAMB-3. For oxidised bitumen, the value of residual penetration is 50%, that is, during heating, the hardness of this sample increases significantly, while for modified samples, their hardness does not increase so rapidly. An increase in residual penetration along with a decrease in SP growth after RTFOT aging indicates that the modified samples have better resistance to aging than the original oxidised bitumen.

Analyzing the initial indicators, as well as the results obtained after technological aging, it can be stated that the most optimal modification temperature is 120 °C, which is confirmed by the initial P25 values, which is the highest for the HAMB-1 sample and is 7.2 mm in comparison with samples HAMB-2 and HAMB-3. Also, for the HAMB-1 sample, the values of D25 and E25 are the best (Figure 1). The values of residual penetration and SP after RTFOT do not differ significantly for HAMB-1 and HAMB-2 indicators, while from a technological point of view it is more appropriate to modify at lower temperatures. Under such conditions, in addition to the positive effect of humic acids on the physical and mechanical characteristics of bitumen, energy costs are reduced.

The results obtained in this work correlate with the results obtained by other authors [35,36].

Pensini et al. [35] looked into how humic acids affected the stability of toluene/water emulsions when bitumen was in the mixture. Bottle testing revealed that emulsions were unstable when bitumen or HA were introduced separately, but they were stable when both substances were present in the mixture at the same time. According to experiments conducted with the oscillating barrier method using a Langmuir trough and an interfacial shear rheometer, the synergistic interactions between HA and bitumen produced interfacial films with high compressional and shear visco-elastic modules, which were used to explain the stability of the mixed HA/bitumen system. At pH 3, 5.5, and 10, the shear rigidity of HA and bitumen films was measured, and it was established that there was a noticeable pH dependence.

At pH = 3, where the electrostatic repulsion between HA and bitumen was probably less intense than at pH 5.5 and 10, the shear visco-elastic modules were at their maximum. As observed in situ using Brewster Angle Microscopy at the toluene-water interface, HA not only altered the stiffness of the bitumen coatings but also their shape [35].

Bitumen became more hydrophilic as pH rose, according to the results of contact angle measurements on fresh and oxidized bitumen samples [36]. It was established that, even though just a small amount of humic acids were produced in the bitumen during the artificial oxidation process, bitumen's hydrophobicity significantly diminished. The impact of additional humic acids on bitumen's wettability was also assessed. At pH 3, it was defined that the presence of humic acids greatly reduced the contact angle of bitumen; however, at pH 7 and 10, the effect of humic acids was not significant. Compared to the impact of artificial bitumen oxidation, the impact of humic acids on bitumen wettability at pH 7 was minimal. Thus we established that humic acids, if present in the internal or surface structure of bitumen, cause it to become hydrophilic. However, when introduced as free chemicals, they have a negligible impact, especially in neutral and alkaline pH conditions, which also suggests that there is little humic acid adsorption from solution onto bitumen.

4. Conclusions

Based on the results of the modification, we determinate that:

- lignite processing produces humic acids, which have reactive phenolic and carboxyl functional groups that make them good at changing the properties of petroleum bitumens;
- as the temperature of the modification process increases, the heat resistance increases and the elastic properties of the bitumen samples improve, while the plasticity decreases and the hardness increases, i.e., the bitumen partially loses its binding properties;
- addition of humic acids in the amount of 2.0 wt.% makes it possible to significantly improve the resistance of bitumen samples to technological aging compared to the original binder in particular, the residual penetration for all modified samples increases significantly, and the softening temperature of these samples does not increase so rapidly after technological aging according to the RTFOT method;
- the optimal modification temperature is 120 °C, which is confirmed by the values of the initial penetration, which is the highest for the HAMB-1 sample and is 7.2 mm compared to HAMB-2 and HAMB-3 samples. Also, for the HAMB-1 sample, the values of ductility and elasticity determined at 25 °C are the best;
- the temperature of the modification process at the of 120 °C is also justified from the technological point of view, since during the mixing of bitumen with humic acids, the loss of volatile components during the interaction of the mixture components decreases.

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