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PRODUCTION OF BITUMEN MODIFIED WITH LOW-MOLECULAR ORGANIC COMPOUNDS FROM PETROLEUM RESIDUES. 4. DETERMINING THE OPTIMAL CONDITIONS FOR TAR MODIFICATION WITH FORMALDEHYDE AND PROPERTIES OF THE MODIFIED PRODUCTS

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Abstract. The effect of factors on the process of chemical modification of tar with formaldehyde using a sulfuric acid as the catalyst has been studied. By using experimental results, the adequate statistical-mathematical (ESM) model has been developed. Based on this model, the optimal values on the process of chemical modification of tar with formaldehyde using a sulfuric acid as the catalyst have been identified, bringing about optimal penetration value and softening point of the modified tars. Data predicted on the basis of the ESM model were compared with empirical evidence about modified tars preparation.

Keywords: tar, formaldehyde, optimal conditions, experimental statistical-mathematical (ESM) model.

1. Introduction

Nowadays, the quality of binders used in bitumen production is the important factor to improve the operational properties of road pavement. One of the most prospective way to increase the binder quality is its modification with various polymers.[1,2] Depending on the modifier nature and method of its introduction into bitumen, different polymers are used: elastomers, thermoplastics, thermosetting plastics, thermoplastic elastomers and others.[2-5]

Apart from the mentioned compounds, crumb rubber is added to bitumen in order to reduce noise during traffic, as well as to prevent the formation of cracks during asphalt shrinkage in winter and plastic deformation in summer. Crumb rubber is obtained due to the grinding of used tires.[6,7] It was found that the size of crumb rubber particles should not exceed 0.35 mm and its amount in the modified bitumen should be in the range of 5–9 wt%.

To improve the adhesive properties of bitumen it is proposed to use the functional resins.[8-15] The peculiarity is that the resins contain different by nature functional groups (epoxy, peroxy, hydroxy, *etc.*) in their structure, which may react with bitumen component and form the cross-linked structures. This gives the possibility to increase the adhesive properties of commercial bitumen by 1.5–2 times.

The interesting approach is bitumen production due to tar chemical modification with low-molecular compounds, with formaldehyde[16,17] or maleic anhydride,[18] in particular. According to this approach, it is unnecessary to modify the obtained bitumen with polymers or resins because its modification occurs due to the chemical modification of tar. If formaldehyde is used, it reacts with aromatic compounds of tar. The formed arene-formaldehyde resins are modifiers of bitumen properties on the one hand, and on the other hand, the transition of oils into resins takes place,[19] which also improves the bitumen properties. When petroleum residue is modified with maleic anhydride,[18] the molecules of anhydride react with bitumen components. This also allows to improve the bitumen properties due to the additional introduction of compounds with hydroxy groups.[20]

This work is a continuation of study described by us previously.[19] The aim of this work is to determine the optimum conditions for chemical modification of tar with formaldehyde. To define optimal conditions for chemical modification of tar with formaldehyde, a series of experiments was carried out. The development of experimental statistical-mathe-matical (ESM) model was justified by this empirical evidence. This model covers dependencies of main response functions on the process factors, and on its basis the optimal conditions of chemical modification of tar with formaldehyde can be predicted.

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2. Experimental

2.1. Materials

Tar produced by JSC Ukrtatnaphta (Kremenchuk, Ukraine) was used as a raw material. Its characteristic is presented in the previous work.[19] Formaldehyde was used as 37% aqueous solution (formalin). The catalysts were concentrated sulfuric acid (density 1.83 g/cm^3) and concentrated hydrochloric acid (density 1.19 g/cm^3).

2.2. Experimental Procedure

Tar modification with formaldehyde was caried out according to the procedure described previously.[19] The conditions and main characteristics of the formaldehyde modified tars (FMT) are represented in Table 2.

Table 1. Physico-chemical characteristics of BO

Index	Value	Standard or Ref.
Penetration at 298 K, 0.1 mm	82	EN 1426:2015, IDT
Softening point (R&B), K	320.2	EN 1427:2015, IDT
Ductility at 298 K, cm	>150	DSTU 8825:2019
Dynamic viscosity at 333 K, Pa·s	96	DSTU EN 12596:2018
Kinematic viscosity at 408 K, mm^2/s	283	DSTU EN 12595:2018
Flash point (open cup), K	582	DSTU EN ISO 2592:2017
Solubility, %	99.95	DSTU EN 12592:2018
Adhesion to crushed stone, points	3.0	DSTU B V.2.7-81-98
Fraas breaking point, K	261	DSTU EN 12593:2018
Plasticity range, K	332.2	DSTU EN 12607-2:2019
Penetration index	-0.7	DSTU 4044:2019

Table 2. Conditions for obtaining FMT and their main characteristics

Index	FMT-1	FMT-2	FMT-3
Formalin amount (including formaldehyde) per 100 g of tar, wt %	1.0 (0.37)	1.9 (0,70)	3.0 (1,11)
Catalyst and its amount per 100g of tar, wt%	H_2SO_4 1.1	H_2SO_4 1.7	H_2SO_4 3.2
Formalin: catalyst ratio, w/w	0.91	1.12	0.94
Temperature, K	383.0	378.0	383.0
Time, h	0.6	0.6	0.8
Penetration at 298 K, 0.1 mm	144	89	47
Softening point (R&B), K	321.0	332.0	356.4

2.3. Methods of Analyses

The analysis of *physico-technological indicators* of the initial materials and resulting products was carried out using the standard methods:

- ✓ softening point (R&B) – according to EN 1427:2018;
- ✓ penetration – according to EN 1426:2018;
- ✓ adhesion to crushed stone – according to Gunka *et al.*[15];
- ✓ Fraas breaking point – according to EN 12593:2018;
- ✓ Penetration index was calculated using formula (1);
- ✓ Plasticity range was calculated using formula (2);
- ✓ Rolling bottle test – according to EN 12697-11:2018;
- ✓ Elasticity – according to EN 13398:2018

$$PI = \frac{20SP + 500\lg P - 1952}{SP - 50\lg P + 120} \quad (1)$$

where PI is penetration index at 298 K; SP is softening point; P is penetration, 0.1 mm.

$$PR = SP - BP \quad (2)$$

where PR is plastic range, K; SP is softening point, K; BP is brittle point, K.

2.4. Calculation of Experiments Reproducibility and Adequacy of Experimental-Statistic Model

To assess the adequacy of the obtained regression equations, the experimental factors (X_1–X_4) were inserted into equations and expected values of response functions (Y_{ij}^{reg}) were found.

$$\Delta Y_{ij} = Y_{ij}^{reg} - Y_{ij} \quad (3)$$

where Y_{ij} are experimental values; Y_{ij}^{reg} are values of response functions calculated according to the regression equations; i is a response function number (criterion, parameter; $i = 1, 2, 3$); j is an experiment number.

The model adequacy was assessed by the following parameters: a mean relative error of approximation (ε_i); a determination coefficient (R_i^2); Fisher criterion (F_i) and a statistical criterion (F_{r_i}).

The mean relative error of approximation was calculated according to formula (4):

$$\varepsilon_i = \frac{1}{n}\sum_{j=1}^{n}\left|\frac{Y_{ij} - Y_{ij}^{reg}}{Y_{ij}}\right| \tag{4}$$

where n is a number of experiments.

To verify the multifactor regression model we used Fisher criterion, which was calculated by formula (5):

$$F = \frac{S_{reg_i}^2}{S_{res_i}^2} \tag{5}$$

where $S_{reg_i}^2$ is a variance of experimental response functions relative their mean values; $S_{res_i}^2$ is a residual variance of response functions.

$$S_{reg}^2 = \frac{1}{n-1}\sum_{j=1}^{n}\left(Y_{ij} - \overline{Y}_i\right)^2 \tag{6}$$

$$S_{resit}^2 = \frac{1}{n-m_i}\sum_{j=1}^{n}\left(Y_{ij}^{reg} - \overline{Y_{ij}}\right)^2 \tag{7}$$

where $\overline{Y}_i$ is a mean experimental value of the response function; m_i is a number of coefficients in the regression equation.

In accordance with the mentioned calculations the value of Fisher criterion must be larger than a table value at a significance level α and number of degrees of freedom $(n - 1)$ and $(n - m_i)$. In such a case it shows how many times the spread of results relative to the line of the obtained regression equation changes compared to the spread relative to the mean value.[21]

The determination coefficient R^2, which characterizes the significance of response function dependence on the process parameters and has values from 0 to 1, was calculated as described by Bolshev *et al.*[22]

The statistical criterion F_{r_i}, which is a measure of statistical significance R_i^2, was calculated as:

$$F_{r_i} = \frac{n - k_i - 1}{k_i}\cdot\frac{R_i^2}{1 - R_i^2} \tag{8}$$

where k_i is a number of coefficients of regression equations without free term.

The criterion F_{r_i} was compared with a critical value F_{rcr_i}, which was determined as a table value at a significance level α and number of degrees of freedom k_i and $(n - k_i - 1)$. At $F_{r_i} \le F_{rcr_i}$ the null hypothesis, *i.e.*, insignificant regression equation is accepted. At $F_{r_i} > F_{rcr_i}$ the null hypothesis is rejected, *i.e.*, alternative hypothesis about the significance of regression equation is accepted.

Based on the regression equations the optimum conditions of the process were found by means of enumerative technique (minimal or maximal values of response function).

3. Results and Discussion

3.1. Determination of Optimal Conditions

Previously, we established that tar chemical modification with formaldehyde should be carried out at the temperature of 353–393 K for 1 h with formalin concentration of 5 wt% relative to tar, and sulfuric acid as a catalyst in the amount of 2.5 wt% relative to tar.[19] The experiments were carried out with changing one parameter of the process and remaining other parameters constant, therefore we established only the tendency of parameters effect on the process proceeding and the real optimal conditions could not be determined.

So, in this work we developed the experimental statistical model (ESM), which should give the possibility to establish the dependence of the main response functions on the process parameters and thus to propose the optimal conditions of the process.

The experiments were carried out according to the procedure described in subsection 2.2 using the experimental results obtained by us previously.[19] For this purpose the following ranges of the process main parameters were chosen:

– formalin amount is within 1.0–10.0 wt% relative to tar;
– process temperature is within 333–413 K;
– process time is within 0.5–4.0 h;
– catalyst (H_2SO_4) amount is within 0.25–7.0 wt% relative to tar.

To describe the ESM of the process the following response functions and main parameters were used:

– Y_1 is penetration at 298 K, 0.1 mm;
– Y_2 is softening point (R&B), °C;
– X_1 is a process temperature, °C;
– X_2 is a process time, h;
– X_3 is an amount of formalin, wt% relative to tar;
– X_4 is an amount of catalyst, wt% relative to tar;

To construct the equations (12 and 13) we used the STATISTICA software and experimental data given in Table 6.

$$Y_1 = -0.585819 + 0.017680X_1^2 - 3.367001X_2^2 + 0.513433X_3^2 + 3.605878X_4^2 + 0.406048X_1X_2 - 0.376497X_1X_3 - 0.491145X_1X_4 - 1.79866X_2X_3 - 1.09356X_2X_4 + 2.904851X_3X_4 - 0.234048X_1 - 1.29842X_2 + 19.97568X_3 + 0.800819X_4 \quad (9)$$

$$Y_2 = -0.761574 - 0.012659X_1^2 - 0.068427X_2^2 - 0.188714X_3^2 - 1.63699X_4^2 + 0.720539X_1X_2 - 0.108019X_1X_3 + 0.140590X_1X_4 - 7.12446X_2X_3 - .601060X_2X_4 + 0.160497X_3X_4 + 1.245711X_1 - 1.85191X_2 + 18.6988X_3 + 0.233879X_4 \quad (10)$$

Substituting the values X_1–X_4 into Eqs. (9, 10) the predicted values of the response functions (Y_{ij}^{reg}) and relative errors (ε_1 for Y_1 and ε_2 for Y_2) were found for every experiment (see Table 3). The verification of the model was performed.

Table 3. Experimental data, calculated values of response functions and relative errors

Entry	X_1, °C	X_2, h	X_3, wt%	X_4, wt%	Y_1, 0.1 mm	Y_1^{reg}.,0.1 mm	Y_2, °C	Y_2^{reg}, °C	Relative errors	
									ε_1	ε_2
1	120	3	10	0.5	71	68.0169	48	52.43641	0.0420	0.0924
2	120	3	10	1	46	54.5370	57	59.66193	0.1856	0.0467
3	120	3	10	2.5	35	24.9148	76	76.42751	0.2881	0.0056
4	120	3	10	5	24	11.6032	82	88.00026	0.5165	0.0732
5	120	3	10	7	25	33.4069	83	82.52557	0.3363	0.0057
6	60	3	10	2.5	80	74.4995	48	52.42433	0.0688	0.0922
7	80	3	10	2.5	32	43.8276	78	70.55234	0.3696	0.0955
8	100	3	10	2.5	22	27.2993	81	78.55340	0.2409	0.0302
9	140	3	10	2.5	32	36.6739	70	64.17467	0.1461	0.0832
10	100	0.5	10	2.5	24	10.2347	80	85.51511	0.5736	0.0689
11	100	1	10	2.5	29	17.0077	82	84.19120	0.4135	0.0267
12	100	2	10	2.5	26	25.5135	84	81.44073	0.0187	0.0305
13	100	4	10	2.5	26	22.3651	76	75.52922	0.1398	0.0062
14	100	0.5	1	2.5	54	61.2064	53	61.60066	0.1335	0.1623
15	100	0.5	2.5	2.5	40	46.9350	69	67.70944	0.1734	0.0187
16	100	0.5	5	2.5	27	28.2836	77	76.00359	0.0475	0.0129
17	100	0.5	15	2.5	24	17.8575	91	85.59091	0.2559	0.0594
18	100	0.5	1	1	131	111.2089	49	48.96553	0.1511	0.0007
19	100	0.5	5	5	21	10.0534	88	82.29724	0.5213	0.0648
20	100	0.5	1	0.5	145	131.4822	46	43.11683	0.0932	0.0627
21	100	0.5	2.5	1.25	50	82.0303	58	57.39079	0.6406	0.0105
22	100	0.5	1	0.25	152	142.2950	42	39.88554	0.0638	0.0503
23	100	0.5	2	0.625	105	111.0273	48	48.52168	0.0574	0.0109
24	100	0.5	5	1.25	40	54.3013	65	65.18339	0.3575	0.0028
25	100	0.5	15	3.75	25	39.4189	90	93.30174	0.5768	0.0367
Average relative errors of approximation (ε)									0.2565	0.0460

When verifying the model, the following regularities were found.

The main part of residues $\Delta Y_{ij} = Y_{ij}^{reg} - Y_{ij}$ represented in histograms and probit plots (Figs. 1-4) are concentrated around zero, which indicates the first mandatory sign of equations adequacy.

The mean relative errors of approximation are: $\varepsilon_1 = 0.2565$ (25.65 %); $\varepsilon_2 = 0.0460$ (4.60 %). According to Tsegelyk,[21] the high precision of prediction is at ε = 0–10 %; the good one at ε = 10–30 % and the satisfied one at ε = 30–50 %. So, the constructed model has a high precision of prediction.

The calculated values of Fisher criterion are:

$$F_1 = 14.09;\ F_2 = 14.86.$$

According to Bolshev *et al.*,[22] at the significance level α=0.05 the critical values are: $F_{1cr} = F_{2cr} = F(0.05; 25; 10) = 2.34$, *i.e.*, they are lower than calculated ones. This again confirms the model adequacy.

The values of determination coefficients are: $R_1^2 = 0.9121$; $R_2^2 = 0.9369$. This means that 91.21 % and 93.69 % of response functions changes (Y_1 and Y_2, respectively) are determined by the process parameters X_1–X_4.

The calculated values of the statistical criterion are: $F_{r1} = 14.09$; $F_{r2} = 14.86$. According to Bolshev *et al.*,[22] at the significance level α=0.05 the critical values of Fisher criterion are equal to $F_{rcr_1} = F_{2cr} = F(0.05; 25; 10) = 2.60$. This indicates the statistical significance of the determination coefficients R_i^2 ($F_{rcr_i} < F_{r_i}$).

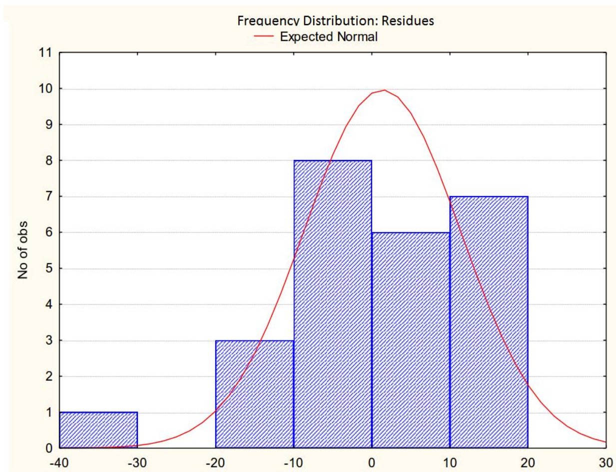

Fig. 1. Histogram of residues ΔY_1

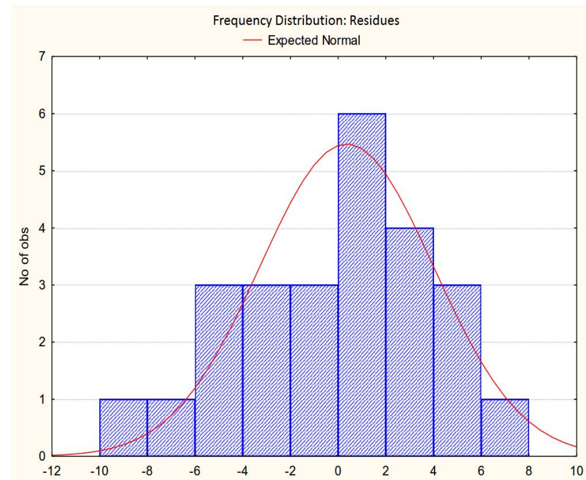

Fig. 2. Histogram of residues ΔY_2

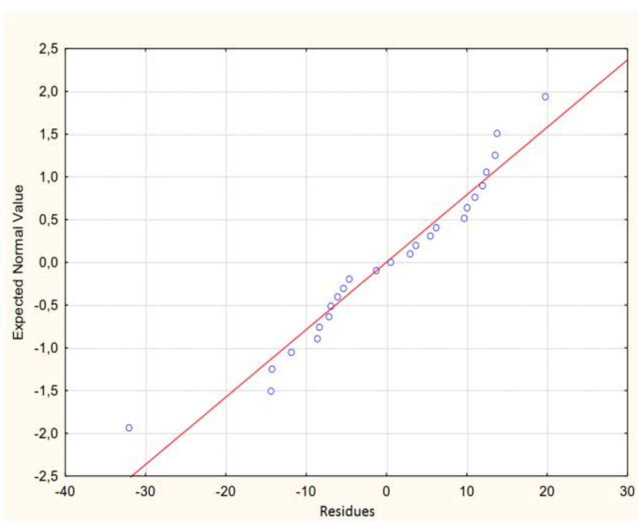

Fig. 3. Probit plot of residues ΔY_1

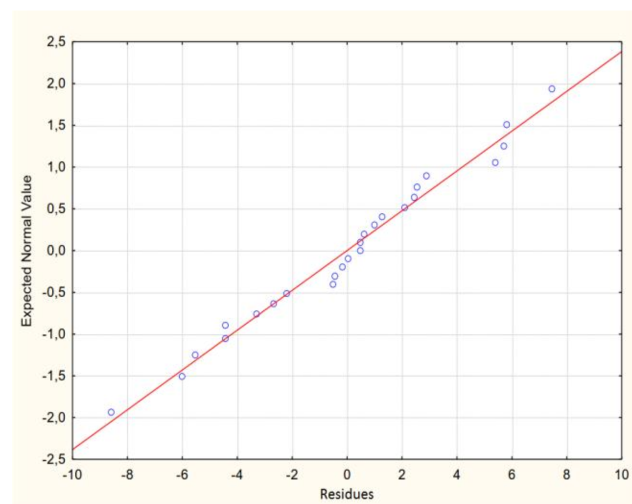

Fig. 4. Probit plot of residues ΔY_2

Table 4. Optimal conditions of the modification process

Symbol	Process parameters				Values of response function			
	X_1, °C	X_2, h	X_3, wt%	X_4, wt%	Y_1, 0.1 mm	Y_1^{reg}, 0.1 mm	Y_2, °C	Y_2^{reg}, °C
Calculated values								
–	110	0.6	1.0	1.1	–	139	–	47.0
–	105	0.6	1.9	1.7	–	88	–	60.6
–	110	0.8	3.0	3.2	–	48	–	80.0
Experimental values (Table 2)								
FMT-1	110	0.6	1.0	1.1	144	–	48.0	–
FMT-2	105	0.6	1.9	1.7	89	–	59.0	–
FMT-3	110	0.8	3.0	3.2	47	–	83.4	–

Table 5. Physico-mechanical properties of the formaldehyde-modified tars

Index	T-1	FMT-1	Requirements for bitumen BND 70/100	FMT-2	Requirements for bitumen BMPA 60/90-53	FMT-3	Requirements for bitumen BMPA 40/60-68
Penetration at 298 K, 0.1 mm (P_{298})	247	144	from 71 to 100 inclusive	89	from 61 to 90 inclusive	47	from 41 to 60 inclusive
Softening point (R&B), K (SP)	312.0	321.0	from 318 to 324 inclusive	332.0	not less than 326.0	356.4	not less than 341.0
Ductility at 298 K, cm (D_{298})	58.1	42.0	not less than 60.0	16.0	not less than 15.0	4.0	not less than 12.0
Elasticity at 298 K, % (E_{298})	–	3.5	not standardized	12.5	not less than 55.0	–	not less than 70.0
Fraas breaking point, K (BP)	255.0	256.0	not above 260.0	258.0	from 253.0 to 259.0	264.0	from 253.0 to 259.0
Penetration index	0.15	0.53	from -2 to 1	1.14	not standardized	2.74	not standardized
Plasticity range, K	330.0	338.0	not standardized	347.0	not standardized	365.4	not standardized
Adhesion to crushed stone, points	2.5	3.5	not standardized	4.5	not less than 3.0	5.0	not less than 3.0

The obtained results confirm the adequacy of developed ESM, statistical significance of the results obtained and the strong relation between response functions and chosen parameters of the process.

The optimal conditions of the tar chemical modification with formaldehyde were found based on Eqs. (9, 10) using the enumerative technique. The optimal conditions will provide a necessary softening point together with maximal penetration:

FMT-1: $Y_1 \rightarrow max$; $Y_2 \geq 47$

FMT-2: $Y_1 \rightarrow max$; $Y_2 \geq 60$

FMT-3: $Y_1 \rightarrow max$; $Y_2 \geq 80$

The calculated optimal values of the process parameters and the calculated (predicted, Y_i^{reg}) values of the response functions are represented in Table 4.

If we compare the results represented in Tables 2 and 4 we observe the minor difference between experimental and predicted values which confirms the right choice of the process optimal conditions represented previously.[19]

3.2. Physico-Mechanical Properties of the Modified Tars

The determined physico-mechanical properties of the formaldehyde-modified tars are represented in Table 5. The properties of original tar (JSC Ukrtatnafta, Kremenchuk, Ukraine) used for the production of FMT-1, FMT-2 and FMT-3 were studied for the comparison.

One can see from Table 5 that the original tar T-1, as it was expected, does not meet the requirements for the binder of asphalt, *i.e.*, bitumen of BND 70/100 grade. FMT-1 does not meet the requirements for P_{298} and D_{298}. The P_{298} values are higher than standard ones; this provide high elasticity of the resulted bitumen, which is achieved in the industry due to the bitumen modification with rubber.

FMT-2 and FMT-3 meet all requirements (except E_{298}) for polymer modified bitumen and correspond to the grade BMPA 60/90-53 and BMPA 40/60-68, respectively (Table 5). At the same time, it should be noted that SP values of FMT-2 and FMT-3 are considerably higher than the standard ones.

4. Conclusions

The optimal conditions of the tar modification with formaldehyde in the presence of H_2SO_4 as a catalyst were determined on the basis of investigated process parameters by means of mathematical simulation. This knowledge allows to produce different grades of pavement bitumen. The results obtained confirm the adequacy of the developed model, statistical significance of the results and the presence of strong relation between response functions and process parameters. A complete analysis of tars synthesized under optimal conditions was performed. The analysis results confirm the improvement of operational characteristics of the obtained products.

It was also found, that at the same value of softening point the formaldehyde modified tars have higher values of penetration to compare with common bitumen. This means that the synthesized product has higher plasticity, what is a great advantage.

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ОДЕРЖАННЯ БІТУМУ, МОДИФІКОВАНОГО НИЗЬКОМОЛЕКУЛЯРНИМИ ОРГАНІЧНИМИ СПОЛУКАМИ ІЗ НАФТОВИХ ЗАЛИШКІВ. 4. ВСТАНОВЛЕННЯ ОПТИМАЛЬНИХ УМОВ ПРОЦЕСУ МОДИФІКУВАННЯ ГУДРОНУ ФОРМАЛЬДЕГІДОМ ТА ВЛАСТИВОСТІ МОДИФІКОВАНИХ ПРОДУКТІВ

***Анотація**. Досліджено вплив чинників на перебіг процесу хімічного модифікування гудрону формальдегідом з використанням як каталізатора сульфатної кислоти. Використовуючи експериментальні дані, розроблено адекватну експериментально-статистичну математичну (ЕСМ) модель та на її основі встановлено оптимальні значення чинників процесу хімічного модифікування гудрону формальдегідом з використанням як каталізатора сульфатної кислоти, які забезпечують оптимальні значення пенетрації та температури розм'якшеності модифікованих залишків. Порівняно прогнозовані на основі ЕСМ та практичні дані процесу модифікування залишків.*

***Ключові слова**: гудрон, формальдегід, оптимальні умови, експериментально-статистична математична модель.*