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DEVELOPMENT OF MATHEMATICAL MODEL AND IDENTIFICATION OF OPTIMAL CONDITIONS TO OBTAIN PHENOL-CRESOL-FORMALDEHYDE RESIN

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Abstract. The effect of factors on the process of obtaining phenol-cresol-formaldehyde resin (PhCR-F) has been studied. By using empirical evidence, the adequate experimental statistical-mathematical (ESM) model has been developed. Based on this model, the optimal values of the process factors for obtaining PhCR-F have been identified, bringing about both high yield and softening point of the resin. Data predicted on the basis of the ESM model were compared with empirical evidence about PhCR-F preparation.

Keywords: phenol-cresol-formaldehyde resin, optimal conditions, experimental statistical-mathematical (ESM) model, modifier, bitumen.

1. Introduction

At present, due to increasing traffic volumes common asphaltic concrete based on unmodified bitumen is not able to provide desired physical and mechanical properties as well as durability of road surfaces. One of the directions in enhancing the quality of bitumen for making road pavements with good performance characteristics is to improve the structure and properties of bitumens by modifying them with polymeric materials.

For modification of road bitumens, thermoplasts are most commonly used (mainly, SBS-type styrenic block-copolymers) owing to their capability not only to increase the bitumen strength, but also impart elasticity to a polymer bituminous mixture, specifically at lower temperatures, and also increase adhesion of bitumen with a mineral material. The content of such polymers in modified bitumens may account for 3–10 wt % [1-5].

The main disadvantage restricting the growth rate of producing thermoplastic elastomer-modified bitumen is their high cost (1.5–2.5 times greater than the cost of unmodified bitumen) [1, 2]. It is, therefore, important to search for inexpensive substances that improve the performance of bitumens and, primarily, their adhesive properties.

At the Department of Chemical Technology of Oil and Gas Processing, Lviv Polytechnic National University, the possibility of using modified phenol-formaldehyde resin (PFR) as additives to petroleum bitumen was trailed [13-16]. These studies show that the said resin has proved to improve a range of performance characteristics of bitumens, most notably, the adhesion.

Consequently, the idea was put forward to investigate the use of PFR derived from relatively cheap raw materials. The phenolic fraction was used as a feedstock collected from coke and chemical plants in Ukraine. Additionally, feedstock contains relatively large amounts of cresols; therefore, accordingly, phenol-cresol-formaldehyde resins (PhCR-F) were yielded. In publications reported by authors [6-7], the manner PhCR-F is obtained from a phenolic fraction and the application of PhCR-F as modifiers of bitumen was investigated.

While using this modifier, a significant enhancement is observed in the adhesive properties of the domestic petroleum bitumens, enabling a strong relationship between a film of bitumen and a surface of mineral materials. This allows to extend the life of the road surface and to significantly improve its durability.

To define optimal conditions of the mechanism of PhCR-F preparation, a series of experiments was carried out. The development of experimental statistical-mathematical (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 obtaining PhCR-F can be predicted.

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2. Experimental

As a feedstock a phenolic fraction, collected from JSC "Zaporizhkoks" (Ukraine) was used. Its performance characteristics are provided in Table 1.

According to the Scheme (Fig. 1) the "raw" (technical) phenols were extracted from a feedstock and undergone polycondensation with formaldehyde.

Phenols from the phenolic fraction were removed using 20% NaOH solution. This removal is based on the reaction of phenols and alkali with the formation of water-soluble phenolates, which are converted into phenols with a concentrated hydrochloric acid. The yield of "raw" phenols from the phenolic fraction was 32.3 wt %.

The process of phenol polycondensation with formaldehyde was carried out following a procedure given in [8]. A starting material was placed into a three-necked reactor and while stirring heated to a predefined temperature in a thermostat. A required amount of formalin (the content of formaldehyde in formalin was 37 %) coupled with the concentrated hydrochloric acid (a catalyst) was further added, and then the onset of the process was recorded. On completion of the synthesis, the hot reaction mixture, prepared from "raw" phenols, was poured into a beaker. Then, after cooling the aqueous phase was drained off, and the resin was dried in a vacuum oven for 3 h at 373 K.

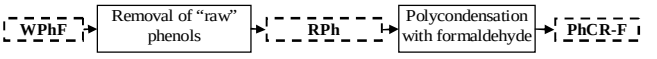

Fig. 1. Scheme of the research: WPhF – wide phenolic fraction; RPh – "raw" (technical) phenols; PhCR-F – phenol-cresol-formaldehyde resin

Table 1

Characteristics of a starting material

Indices	Values
Distillation, K:	
Initial boiling point	378
10% distilled at the temperature	437
20 % distilled at the temperature	445
30 % distilled at the temperature	447
40 % distilled at the temperature	450
50 % distilled at the temperature	452
60 % distilled at the temperature	455
70 % distilled at the temperature	458
80 % distilled at the temperature	470
90 % distilled at the temperature	475
95 % distilled at the temperature	481
Bromine number, gBr_2/100 g product	81.64

Table 2

Characteristics of oxidized road bitumen

Index	Values for oxidized bitumen BND 60/90
Penetration at 298 K, m·10^{-4}	70
Softening point R&B, K	319
Ductility at 298 K, m·10^{-2}	63
Adhesion to glass, %	33
Adhesion to crushed stone, points	3
Change in properties after heating:	
mass loss, %	0.1
residual penetration, %	93
change in softening temperature, K	2
Fraass breaking point, K	255
Penetration index	–1.5
Plasticity range, K	337

The main factors affecting the polycondensation of "raw" phenols with formaldehyde are the concentration of a catalyst, the mass ratio of components, the temperature, and the process time.

Road bitumen, whose characteristics are represented in Table 2, was used for the experiments.

The polymer modified bitumen (PMB) was prepared as follows: the definite amount of bitumen was heated to a fixed temperature, and then a modifier (2.4 wt %) was added. The mixture was stirred (Re = 1200) at 463 K for 1 h.

The quality indices of the initial and modified bitumen were determined using standard methods.

3. Results and Discussion

It was necessary to develop the ESM model of the process of PhCR-F preparation, verify the adequacy of the former, and find the optimal process conditions. By analyzing experimental data, the intervals that change the main factors of the process have been selected for the ESM model development, such as the catalyst concentration of 0–6 wt %; the mass ratio of the components of 1.78–3.80; the temperature of 318–373 K; and the duration of 5–120 min.

In describing the process of obtaining PhCR-F using the ESM model, the following designations were used for the response functions and main control factors of the process: Y_1 is the resin yield, wt %; Y_2 is the ring-and-ball softening point, (ºC); X_1 is the concentration of a catalyst, wt %; X_2 is the mass ratio of components; X_3 is temperature, ºC; X_4 is the process duration, min.

The ESM model was devised according to the results of the study, presented in Table 2. For the response functions, various types of dependencies on the process factors were developed and, finally, resulting in the choice of non-linear models as they showed the best fit to the experimental data. For defining the equations of multiple regressions (1) and (2), the STATISTICA software package was used.

$$\begin{gathered} Y_1 = -41.7817 - 1.19464 \cdot X_1^2 - 8.63368 \cdot X_2^2 + \\ +0.001537 \cdot X_3^2 - 0.001700 \cdot X_4^2 - 211.626 \cdot X_1 \cdot X_2 - \\ -1.90101 \cdot X_1 \cdot X_3 + 11.65319 \cdot X_1 \cdot X_4 + \\ +4.327906 \cdot X_2 \cdot X_3 + 5.019971 \cdot X_2 \cdot X_4 - \\ - 0.293050 \cdot X_3 \cdot X_4 - 121.787 \cdot X_1 - 72.6620 \cdot X_2 + \\ + 15.872311 \cdot X_3 - 14.2770 \cdot X_4 \end{gathered} \quad (1)$$

$$\begin{gathered} Y_2 = -30.3736 - 2.19792 \cdot X_1^2 - 3.70991 \cdot X_2^2 + \\ + 0.007490 \cdot X_3^2 - 0.005547 \cdot X_4^2 - 154.004 \cdot X_1 \cdot X_2 - \\ - 1.40209 \cdot X_1 \cdot X_3 + 8.707432 \cdot X_1 \cdot X_4 + \\ + 2.707432 \cdot X_2 \cdot X_3 + 3.537820 \cdot X_2 \cdot X_4 - \\ - 0.2113198 \cdot X_3 \cdot X_4 - 88.5967 \cdot X_1 - 52.8532 \cdot X_2 + \\ + 11.80819 \cdot X_3 - 10.0859 \cdot X_4 \end{gathered} \quad (2)$$

By substituting the values of X_1-X_4 in all the above equations, the expected values of the response functions (Y_{ij}^{reg}) and relative ESM errors (ε_1 for Y_1; ε_2 for Y_2) were found for each experiment. Table 3 lists all these values. The models' adequacy was checked using regression response functions.

The parameters, including the average relative errors of approximation (ε_i), coefficient of determination (R_i^2), Fisher (F_i) and statistical criteria (F_{r_i}), were used to check the adequacy of the models.

The average relative error of approximation was calculated by the formula:

$$e_i = \frac{1}{n} \sum_{j=1}^{n} \left| \frac{Y_{ij} - Y_{ij}^{reg}}{Y_{ij}} \right| \quad (3)$$

where n is a sample size (a number of experiments), Y_{ij} are the observed parameter values obtained during the experiment, Y_{ij}^{reg} are the values of the response functions defined from the regression equations, i is the number of the response function, and j is the number of experiment.

For checking the adequacy of a multifactor regression model, the Fisher criterion (F_i) was employed and calculated by the formula:

$$F_i = \frac{S_{reg_i}^2}{S_{resit_i}^2} \quad (4)$$

where $S_{reg_i}^2$ the variance of the experimental response functions relative to their mean; $S_{resit_i}^2$ denotes the residual variance of response function.

$$S_{reg}^2 = \frac{1}{n-1} \sum_{n-1}^{n} (Y_{ij} - \overline{Y_i})^2 \quad (5)$$

where $\overline{Y}_i$ is an average experimental value of response function.

$$S_{resit}^2 = \frac{1}{n - m_i} \sum_{j-1}^{n} (Y_{ij}^{reg} - \overline{Y_{ij}})^2 \quad (6)$$

where m_i means the number of coefficients in the regression equation.

Such a calculation scheme suggests that the Fisher criterion must be greater than the tabular (critical) one at the level of significance α and degrees of freedom $(n - 1)$ and $(n - m_i)$. In this case, it shows how many times the scattering of results changes relative to the line of the resulting regression equation as compared to scattering as to the mean value [9].

The coefficient of determination (R^2), which is representative of the significance of the dependence of response functions on the process factors and assumes the values from 0 to 1, was defined by the standard methods [10].

Table 3

Experimental data, calculated values of response functions and relative errors

Entry	X_1, wt %	X_2	X_3, °C	X_4, min	Y_1, wt %	Y_1^{reg}, wt %	Y_2, °C	Y_2^{reg}, °C	Relative errors	
									ε_1	ε_2
1	0	1.78	100	60	69.3	72.89	58	75.00	0.0518	0.2931
2	1	1.78	100	60	88.5	82.30	119	92.31	0.0700	0.2243
3	2	1.78	100	60	90	89.33	115	105.23	0.0074	0.0849
4	3	1.78	100	60	94.3	93.96	110	113.75	0.0035	0.0341
5	6	1.78	100	60	94.3	93.53	117	112.95	0.0081	0.0346
6	3	1.78	100	60	94.3	93.96	110	113.75	0.0035	0.0341
7	3	2.2	100	60	88.5	90.22	95	94.18	0.0195	0.0086
8	3	2.72	100	60	81.9	81.36	82	68.14	0.0065	0.1691
9	3	2.86	100	60	79.4	78.18	60	60.78	0.0153	0.0131
10	3	3.05	100	60	73.3	73.32	47	50.57	0.0003	0.0759
11	3	3.3	100	60	65.2	65.98	23	36.72	0.0120	0.5966
12	3	3.8	100	60	48.12	48.05	14	7.63	0.0013	0.4547
13	3	1.78	45	60	75.5	74.94	74	74.39	0.0074	0.0053
14	3	1.78	60	60	78	79.21	82	80.63	0.0155	0.0166
15	3	1.78	80	60	86.4	85.97	91	94.20	0.0050	0.0352
16	3	1.78	90	60	90.4	89.81	106	103.23	0.0065	0.0262
17	3	1.78	95	60	92.5	91.85	109	108.30	0.0070	0.0064
18	3	1.78	100	60	94.3	93.96	110	113.75	0.0035	0.0341
19	3	1.78	100	5	82.5	82.82	79	77.82	0.0039	0.0150
20	3	1.78	100	10	86.5	84.26	84	82.47	0.0259	0.0182
21	3	1.78	100	20	85.8	86.88	89	90.95	0.0126	0.0219
22	3	1.78	100	40	86.3	91.10	96	104.57	0.0557	0.0893
23	3	1.78	100	60	94.3	93.96	110	113.75	0.0035	0.0341
24	3	1.78	100	90	93.8	95.71	113	119.21	0.0204	0.0550
25	3	1.78	100	120	94.6	94.39	116	114.68	0.0022	0.0113
Average relative errors of approximation (ε)									0.0147	0.0957

The statistical criterion (F_{r_i}), which is a measure of statistical significance R_i^2, is given by the formula below:

$$F_{r_i} = \frac{n - k_i - 1}{k_i} \cdot \frac{R_i^2}{1 - R_i^2} \quad (7)$$

where k_i is the number of coefficients of the regression equation without an intercept term.

The calculated value F_{r_i} was compared with the critical value F_{rcr_i} as shown in the tables at the level of significance α together with the degrees of freedom, such as k_i and $(n - k_i - 1)$. When $F_{r_i} > F_{rcr_i}$, it may be argued about the statistical significance of the regression equation.

When making an evaluation of the adequacy of Eqs. (1) and (2), the patterns below were established.

The major portion of residuals $\Delta Y_{ij} = Y_{ij}^{reg} - Y_{ij}$ as shown in histograms and plots of probit (Figs. 2-5) is centered around zero, signifying the first mandatory characteristic of the normality of resulting equations.

The average relative errors of approximation are as follows: ε_1 = 0.0147 (1.47 %), ε_2 = 0.9566 (9.56 %). As reported in [11] at ε = 0–10 % the precision of prediction is high, at ε = 10–20 % it is good, and at ε = 20–50 % it is satisfactory. From this it can be claimed that the built models are in good agreement with experimental evidence.

The estimated values of the Fisher criterion are F_1 = 22.53 and F_2 =7.54. According to the table of Fisher criterion values [12], at the level of significance α of 0.05 the critical values are defined as $F_{1cr} = F_{2cr} = F(0.05; 24; 10)$ = 2.74. That is, they are less than that calculated, which also proves the normality of the model.

The coefficients of determination are R_1^2 = 0.9693 and R_2^2 = 0.9135. In other words, 96.93 % and 91.35 % of changing a response function (Y_1 and Y_2, respectively) are determined using the preferred control factors of the process (X_1–X_4).

The estimated values of the statistical criterion are F_{1r} = 22.53 and F_{2r} = 7.54. As shown in the table of Fisher criteria, the critical values are given as $F_{1rcr} = F_{2rcr} = F(0.05; 14; 10)$ = 2.86 at the level of significance α of 0.05. This clearly demonstrates the statistical significance of coefficients of determination R_i^2 ($F_{ircr} < F_{ir}$).

The average relative errors of approximation are as follows: ε_1 = 0.0147 (1.47 %), ε_2 = 0.9566 (9.56 %).

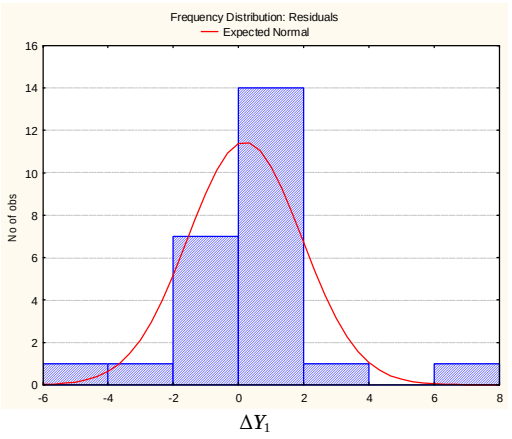

Fig. 2. Histogram of ΔY_1 residuals

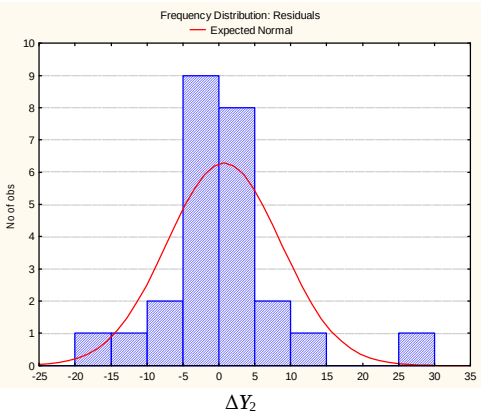

Fig. 3. Histogram of ΔY_2 residuals

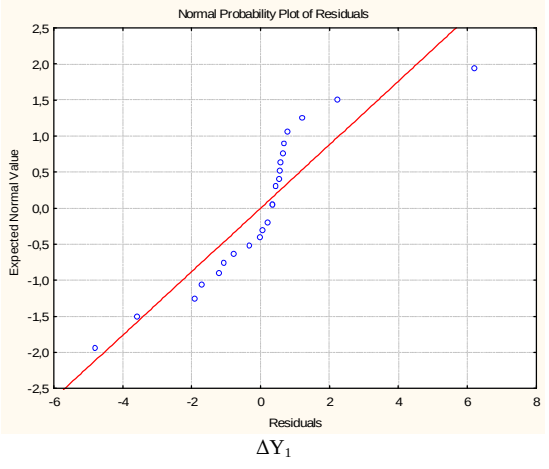

Fig. 4. Plot of probit for ΔY_1 residuals

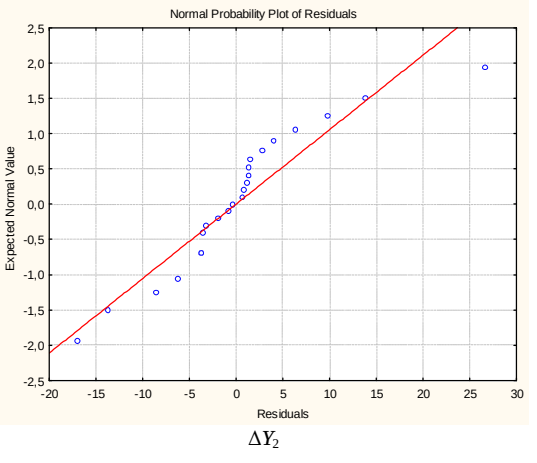

Fig. 5. Plot of probit for ΔY_2 residuals

Table 4

Optimal conditions of PhCR-F synthesis

Process parameters				Response function value			
X_1, wt %	X_2	X_3, °C	X_4, min	Y_1, wt %	Y_1^{reg}, wt %	Y_2, °C	Y_2^{reg}, °C
Calculated values							
1.85	2.15	104.5	69	–	95.0	–	85
Experimental values							
2.06	2.16	105.0	69	92.5	–	92	–

Table 5

Physico-mechanical parameters of pure and modified bitumen

Bitumen	Parameters							
	Softening point R&B, K	Penetration at 298 K, 0.1 mm	Ductility at 298 K, m·10^{-2}	Fraass breaking point, K	Plasticity range, K	Penetration index	Adhesion to	
							crushed stone, points	glass, %
BND 60/90	319	70	63	255	337	-1.5	3	33
BND 60/90 + PhCR-F (1.0 wt %)	321	68	46	255	339	-0.9	5	87

These figures signify the adequacy of the ESM process in which PhCR-F was prepared, the statistical significance of results and the presence of a strong relationship between response functions and preferred control factors of the process.

On the basis of the regression equations, the optimal process conditions were found by the method of uniform search for the values of the response functions and that would ensure the maximum yield of PhCR-F and softening point of the resulting resin.

The calculated optimal values of the process parameters (X_1 = 1.85 wt %; X_2 = 2.15; X_3= 104.5 ºC; X_4= 69 min) and estimated (predicted, Y_i^{reg}) values of response functions are listed in Table 4.

The synthesis of PhCR-F carried out under conditions as close as possible to optimal (X_1 = 2.06 wt %; X_2 = 2.16; X_3 = 105 ºC; X_4 = 69 min) resulted in a sufficiently high yield of the major product (the resin) – 92.5 wt % and its high softening point is 92 °C. The relative difference between the experimental and predicted values amounts to 2.70 % (for Y_1) and 7.61 % (for Y_2).

The resulting resin was used as an adhesive additive to modify oxidized road bitumen. In accordance with industrial requirements the amount of modifier approx. 1 wt % is technically and economically feasible. Therefore, we studied bitumen modification adding 1 wt % of PhCR-F. Characteristics of the obtained PMB are given in Table 5.

One can see from the obtained results that addition of PhCR-F in the amount of 1 wt % to bitumen changes the following characteristics:

– the softening temperature is increased by 2 K;

– elasticity (penetration and ductility) is slightly degraded, though plasticity interval is increased;

– adhesive properties are considerably improved (from 33 to 87 %).

4. Conclusions

A quadratic experimental statistical model of the process to prepare the phenol-cresol-formaldehyde resin from the phenolic fraction of the coal tar has been developed. The adequacy and statistical significance of the model has been proved on the basis of four parameters.

The optimal process conditions were found (X_1 = 1.85 wt %; X_2 = 2.15; X_3 = 104.5 ºC; X_4 = 69 min), and 92 °C softening point of the resin was produced. The resin yield was 92.5 wt % for a starting material.

Applying the developed ESM model, we can fairly accurately predict the amount of the resulting resin and its main characteristic (a softening point by the ring-and-ball method). The resin prepared under predicted conditions based on the ESM model was proved to have a greater yield and a higher softening point than those found in the previous studies. This PhCR-F will be used further for modification of road bitumens and derived bituminous emulsions.

The addition of PhCR-F in the amount of 1 wt % to oxidized road bitumen allows to obtain new product, namely bitumen modified with adhesive additives.

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РОЗРОБЛЕННЯ МАТЕМАТИЧНОЇ МОДЕЛІ І ВСТАНОВЛЕННЯ ОПТИМАЛЬНИХ УМОВ ПРОЦЕСУ ОДЕРЖАННЯ ФЕНОЛО-КРЕЗОЛО-ФОРМАЛЬДЕГІДНОЇ СМОЛИ

Анотація. *Досліджено вплив чинників на перебіг процесу одержання феноло-крезоло-формальдегідної смоли (PhCR-F). З використанням практичних даних розроблено адекватну експериментально-статистичну математичну (ЕСМ) модель. На її основі встановлено оптимальні значення чинників процесу одержання PhCR-F, які забезпечують високі вихід і температуру розм'якшення смоли. Порівняно прогнозовані на основі ЕСМ та практичні дані процесу одержання PhCR-F.*

Ключові слова: *феноло-крезоло-формальдегідна смола, оптимальні умови, експериментально-статистична математична модель, модифікатор, бітум.*