

KINETIC MODEL OF THE PROCESS OF POLYCONDENSATION OF CONCENTRATED PHENOLS OF COAL TAR WITH FORMALDEHYDE

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Abstract. Phenol formaldehyde resins were obtained by polycondensation of concentrated phenols with formaldehyde in the presence of hydrochloric acid. Concentration of phenols is carried out by treating the phenolic fraction of coal tar with an aqueous solution of sodium hydroxide followed by neutralization of water-soluble phenolates with hydrochloric acid. The kinetic dependences of resin yield and softening temperature on the duration of the process at 333, 353, and 373 K were obtained. The order of the reaction was determined and the effective activation energy of this process was determined by a graphical method. In the interval 333–373 K for polycondensation reactions, the equation of the dependence of the resin yield on the temperature and duration of the process was obtained.

Keywords: phenol formaldehyde resins, novolac, hydrochloric acid, kinetics.

1. Introduction

Phenol formaldehyde resins (PhFR) were the first polymers created by man more than 100 years ago.^{1,2} Thousands of other polymers have been synthesized today, hundreds of which are obtained on an industrial scale. But even with a large number of polymers produced by the industry today, PhFRs occupy a significant place in the total volume of global production of synthetic resins. This is primarily due to the cheapness of their production, the availability of raw materials for their production, and the good operational properties of products based on them.^{3,4} The presence of free phenolic or methylol groups in their structure makes it possible to combine with other functional polymers or introduce other functional groups

in their structure, and thereby improve the properties of products with their participation.^{5,9}

A variety of phenols and aldehydes, mainly formaldehyde, serve as raw materials for the production of PhFR.^{10–12}

As phenols, phenol itself is used, cresols, xylenols, resorcinol and other products containing a free phenol group in their structure.^{8,9}

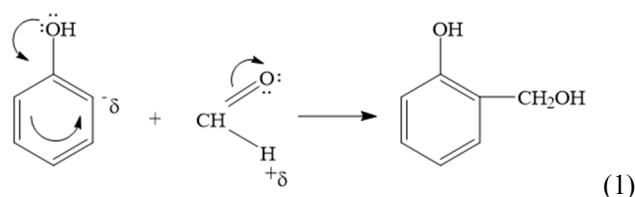
For the first time, phenol and its derivatives were obtained from coal tar, which typically contains 1.5 % of phenolic compounds. This is mainly phenol itself (about 0.5 %), as well as *o*-, *m*-, *p*-cresols, 2,3-, 2,4-, 2,6-, and 3,5-xylenols.¹³

The extraction method is used to isolate the above-mentioned phenols. For this, an 8–12 % aqueous solution of sodium hydroxide is used as an extractant. After the separation of the aqueous solution from the coal tar, it is treated with carbon dioxide and poorly soluble phenol is separated.^{14,15} Also, amides and amines are used to separate phenols from coal processing products.^{16,17}

Phenol and cresols acquired the greatest practical importance for obtaining PhFR.

The polycondensation reaction using the example of phenol itself with formaldehyde is catalyzed by both hydrogen and hydroxyl ions, and given the need to achieve reaction equilibrium, it can be carried out in aqueous solution.

At the first stage of the reaction, there is an electrophilic addition of a formaldehyde molecule in the *ortho*- or *para*-position to the phenolic group with simultaneous rearrangement of the hydrogen atom to the oxygen atom:



In an acidic environment, in which there is no stabilizing effect of hydrogen bonds, the rate of condensation

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reaction of hydroxymethylene groups is quite high and in the case of trifunctional phenol can lead to the formation of a three-dimensional product.¹⁸

To avoid this, the polycondensation reaction is carried out in an acidic medium with an excess of phenol. In practice, a ratio of formaldehyde to phenol equal to 10 : 12 is used. The optimal ratio, which makes it possible to carry out the process safely and obtain a resin with the given properties, is 26.5–27.5 g of aldehyde per 100 g of phenol. This corresponds to an approximate molar ratio of formaldehyde to phenol of 6 : 7.¹⁹ PhFR obtained under these conditions is called novolac resin.

Phenols containing substituents in the *ortho*- or *para*-positions are bifunctional (for example, cresols), and therefore form exclusively linear products when interacting with formaldehyde.

PhFR, due to its availability and ability to combine with other polymers, are used for the production of press materials, coatings, adhesives, as abrasive and friction materials, etc.²⁰

In addition, it is known that PhFRs can serve as effective modifiers of road bitumens. But such PhFRs, which are obtained from pure phenol and are used in road construction, significantly affect the cost of the obtained modified bitumen.^{21–25}

In addition, Ukraine had and will have a large number of coke-chemical industries, the by-product of which is coal tar. Coal tar, as already mentioned, contains a sufficiently large amount of various phenols, and it is practically not used effectively in Ukraine.

Therefore, research related to the use of coal tar as a raw material for the production of phenols from it, with the subsequent synthesis of PhFR based on them, is promising. The resulting PhFRs can serve as polymer additives to improve the properties of road petroleum bitumens.

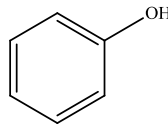
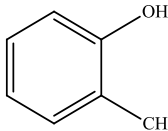
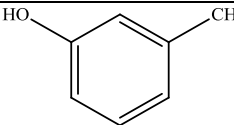
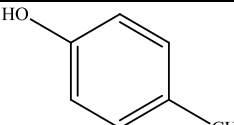
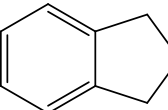
In this article, the kinetic regularities of the reaction of polycondensation of phenol derivatives with formaldehyde in an acidic medium are studied. The obtained results are important for the optimization and technological design of this process.

2. Experimental

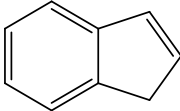
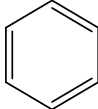
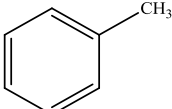
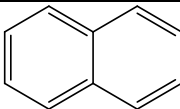
2.1. Materials

To obtain PhFR, we used WPhF, selected at JSC “Zaporizhkoks” (Zaporizhzhia, Ukraine). Determination of the component composition of WPhF and RPh (concentrated phenols) was carried out using chromatographic analysis, which is presented in Table 1. The fractional composition of WPhF is shown in Fig. 1.

Table 1. Component composition of WPhF and RPh

No. s/n	Component	Structural formula	Boiling point (K)	Content (wt.%)	
				WPhF	RPh
1	2	3	4	5	6
1	Phenol		460.87	23.954	33.551
2	<i>o</i> -Cresol		464.00	4.840	14.913
3	<i>m</i> -Cresol		475.00	12.935	37.914
	<i>p</i> -Cresol		474.90		
4	Indan		449.00	2.423	0.120

Continuation of Table

1	2	3	4	5	6
5	Indene		454.60	13.343	0.353
6	Benzene		353.10	3.212	6.719
7	Toluene		383.60	1.894	0.701
8	Naphthalene		491.00	24.866	2.323
9	Unidentified components	–	–	12.533	3.406
	Total	–	–	100.000	100.000

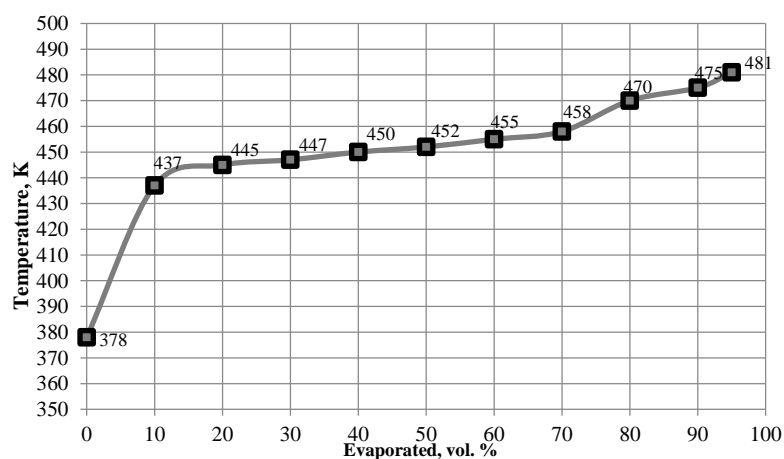


Fig. 1. Distillation curve for WPhF

2.2. Experimental Procedure

The scheme of the process of obtaining phenol formaldehyde resins from WPhF is presented in Fig. 2.

2.2.1. Concentration of "Raw" Phenols

Concentration of phenols from WPhF was carried out using a 20 % aqueous solution of sodium hydroxide. The required amount of WPhF was placed in a dividing funnel, to which was added the required amount of 20 % aqueous NaOH solution (100 g of 20 % aqueous NaOH solution per 100 g of WPhF) and the resulting emulsion was mixed. In the process, phenols interacted with alkali to form water-soluble sodium phenolates. After settling, the mixture was divided into two phases: the upper one – hydrocarbon, which no longer contained phenols; the lower - aqueous, which contained dissolved sodium phe-

molates. The lower (aqueous) phase was poured into a beaker and concentrated hydrochloric acid was gradually added with stirring until the pH of the aqueous phase became acidic (< 7). That is, sodium phenolates were converted into phenols. The mixture from the beaker was poured into a separatory funnel and settled until a constant volume of phases (upper - RPh; lower - water without phenols). The lower (aqueous) phase was drained, and the upper (RPh) was washed several times with hot distilled water until the pH of the aqueous phase was neutral. The yield of RPh from WPhF was 32.3 wt%.

The composition of RPh, which was determined using chromatographic analysis, is presented in Table 1. Analyzing the data in the Table 1, the total content of phenols in WPhF was 41.729 wt %, and the concentration yield from this fraction of phenols was 32.3 wt% (with the total content of phenols – 86.378 wt%).

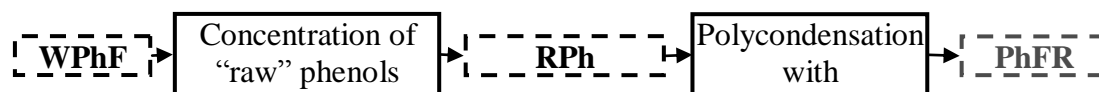


Fig. 2. Scheme of the research: WPhF – wide phenolic fraction; RPh – raw (concentrated) phenols; PhFR – phenol formaldehyde resins

2.2.2. Preparation of Phenol Formaldehyde Resin from Coal Tar

PhFR was obtained by polycondensation of “raw” phenols (separated from WPhF) with formaldehyde. The process of polycondensation was carried out according to the method proposed by Dr. Bratyshak.²⁶ Raw materials were placed in a round-bottom flask with three necks (250 mL) and, with stirring, heated in a thermostat to the temperature of the process, after which the required amount of formalin was added (the mass content of formaldehyde in formalin was 37 wt%) and a catalyst (concentrated hydrochloric acid or crystalline sodium hydroxide). After that, the polycondensation process was carried out with stirring for the required time. After the end of the process, the resulting resin was dried for 3 h at 393 K in a vacuum cabinet. The yield of the obtained resins was determined by the results of weighing the raw materials and the obtained resins.

The yield on RPh was calculated according to the formula, wt%:

$$x = \frac{m_{PhFR} \cdot 100}{m_{RPh}} \quad (2)$$

Yield of reactive components according to the formula, wt %:

$$y = \frac{m_{PhFR} \cdot 100}{m_{RPh} + 0,37 \cdot m_F} \quad (3)$$

where m_{PhFR} , m_{RPh} , m_F are mass of resin, raw material (RPh), and formalin, respectively; 0.37 is mass content of formaldehyde in formalin.

2.2.3. Calculation of the Kinetic Parameters of the Process of Obtaining PhFR

The effective activation energy was calculated similarly to the method proposed by Emanuel.²⁷ A dimensionless value equal to the fraction of unconverted compounds of the starting material was taken as a measure of the reaction rate and was calculated according to the formula:

$$C = 1 - \frac{y}{100} \quad (4)$$

where y is the yield of PhFR on reacting components, wt %.

For second-order reactions, the effective reaction rate constants were calculated using the following formula:

$$k_{ef} = \frac{1}{\tau - \tau_0} \cdot \frac{1}{C - C_0} \quad (5)$$

where C_0 is the initial value of the proportion of unconverted substances in the raw material at the initial reaction duration (τ_0), τ is the reaction duration, s.

The parameters of the Arrhenius equation (k_{0ef} , E_{ef}) were determined by calculation and graphical methods, respectively.

$$k_0 = e^{\frac{\ln(k_{efi} \cdot T_i) - T_i \cdot \ln(k_{efi+1})}{T_i - T_{i+1}}} \quad (6)$$

where k_{efi} , k_{efi+1} – effective rate constants of reactions, at the corresponding temperatures T_i and T_{i+1} .

In the case of fulfilling the Arrhenius equation, the dependence of the effective rate constant on the temperature in the coordinates $\ln(k_{ef}) = f(1/T)$ should be represented by a straight line. In this case, the activation energy can be determined from the tangent of the angle of inclination of the line according to the formula:

$$E_{ef} = -R \cdot \text{tg} \alpha \quad (7)$$

where α is tilt angle; $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ is universal gas constant.

On the basis of the Arrhenius equation and the determined k_{0ef} , E_{ef} , based on formula (5), it is possible to propose a general view of the dependence of the PhFR yield on the temperature and duration of the process.

$$y = 100 - \frac{100}{\frac{1}{C_0} + k_0 \cdot (\tau - \tau_0) \cdot e^{\frac{-E}{R \cdot T}}} \quad (8)$$

2.3. Methods of Analysis

Chromatographic analysis was performed using a gas-liquid chromatograph “Crystal 2000M”. The length of the column is 3 m. Filler - chromaton + 20 % polyphenyl ether.

Principle of operation: exposure at 418 K – 27 min, heating at a rate of 283 K/min to 483 K. Evaporator temperature – 523 K. Detector temperature – 523 K. Gas consumption (helium) – 30 mL/min, hydrogen – 30 mL/min, air – 300 mL/min.

3. Results and Discussions

In order to establish the kinetic regularities of the course of polycondensation reactions of RPh with formaldehyde, the effect of duration on the yield (wt % of RPh and reacting components, Figs. 3 and 4, respectively) of PhFR and its softening temperature (Fig. 5) at different values of the process temperature was studied (333, 353, and 373 K).

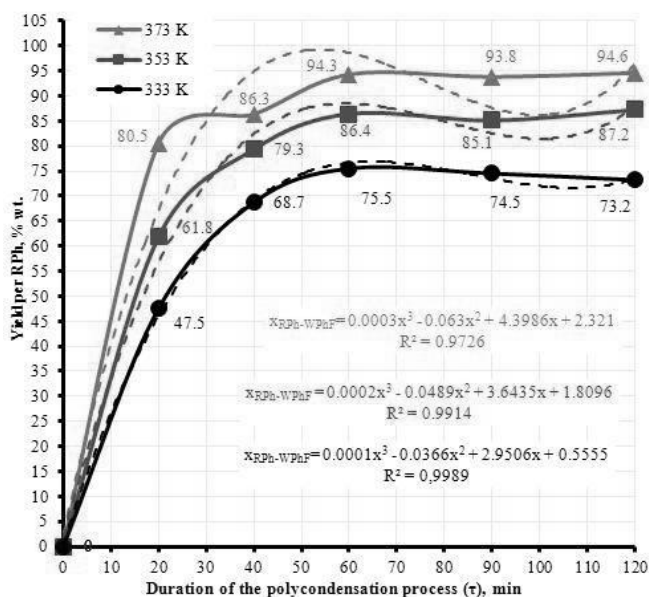


Fig. 3. Effect of process duration on resin yield per raw material (RPh)

According to the obtained data (Figs. 3–5), it can be stated that the process of obtaining PhFR takes place in three main stages:

1) up to 20 min – the beginning of the polycondensation process and the formation of the main amount of resin;

2) 20–60 min – the continuation of the growth of the polymer chain (there is mainly an increase in the SP of the resin);

3) more than 60 min – completion of the process (resin yield and SP remain almost unchanged).

It is worth noting that since PhFR with a high softening temperature can be obtained for a duration of about 60 min, the processing of the obtained results was carried out based on the dependencies of the second stage of the process, in the range of 20–60 min.

Polycondensation reactions of individual substances and mixtures are described by equations of the first, second, and fractional orders.²⁷⁻²⁹ Conversion, the ratio of the initial and current concentration of the polymer, the epoxy number, and the logarithm of the inverse value of the current concentrations of the initial monomer.²⁷

In order to establish the order of RPh polycondensation reactions with formaldehyde using the data shown in Fig. 5, kinetic dependences are constructed, respectively, for the first (Fig. 6) and second orders (Fig. 7).

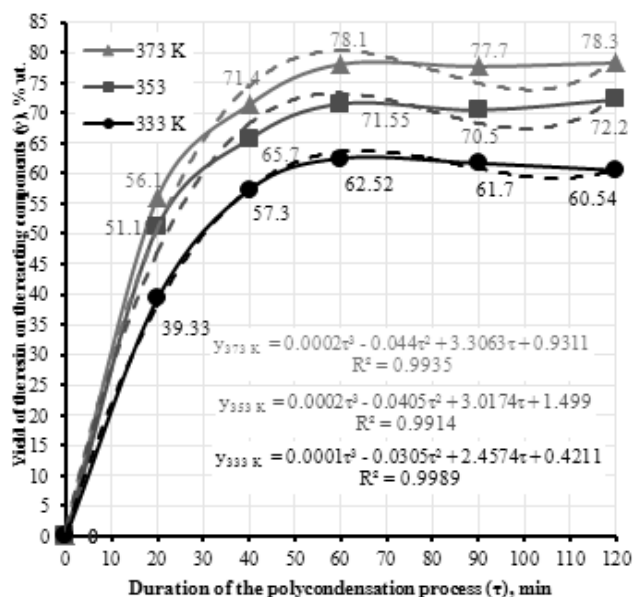


Fig. 4. The effect of the duration of the process on the yield of the resin on the reacting components

It can be seen that the kinetic dependences in Fig. 7 have a more linear character (the average coefficient of determination of straight lines for second-order reactions is 0.9873, and for first-order reactions – 0.9338), so it can be stated that most of the polycondensation reactions of RPh with formaldehyde occur according to the second order.

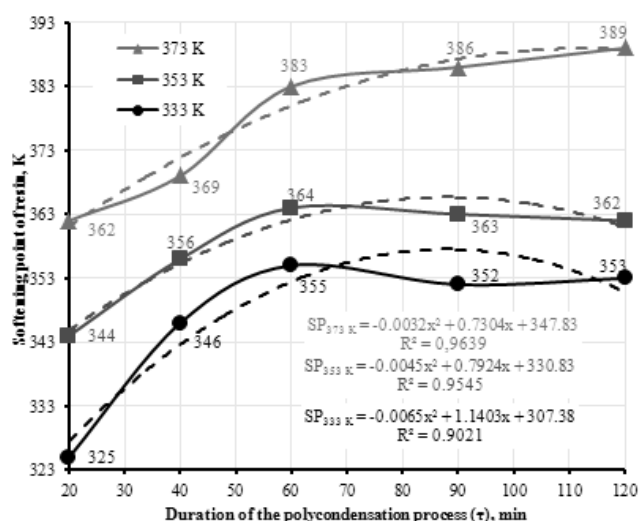


Fig. 5. The effect of the duration of the polycondensation process at 333, 353 and 373 K on the softening temperature of the resin

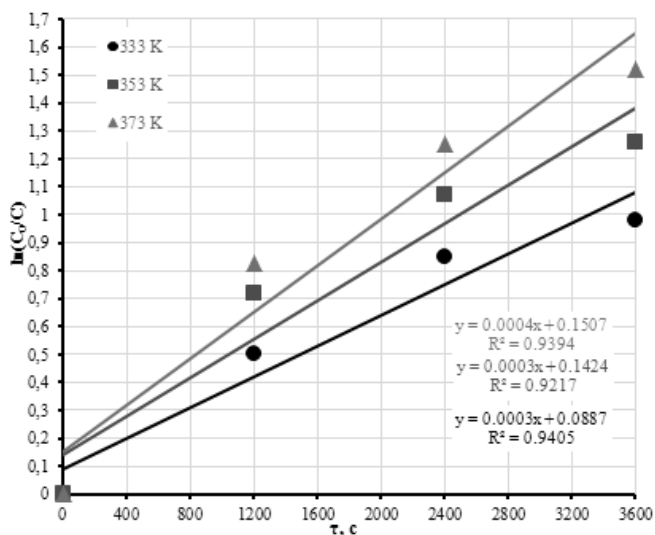


Fig. 6. Dependence of the proportion of unconverted substances (C) on duration (τ) in coordinates $\ln(C_0/C) = f(\tau)$ for first-order reactions

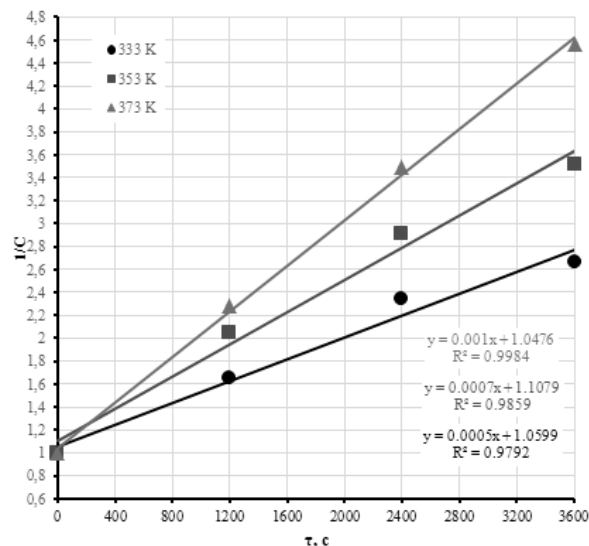


Fig. 7. Dependence of the proportion of unconverted substances (C) on duration (τ) in coordinates $1/C = f(\tau)$ for second-order reactions

Table 2. Calculation of kinetic parameters according to the Arrhenius equation

Temperature interval, K	273–333	333–353	353–373
k_{ef}, s^{-1}	$4.24 \cdot 10^{-4}$	$6.11 \cdot 10^{-4}$	$9.53 \cdot 10^{-4}$
$\ln k_{ef}$	-7.764	-7.401	-6.959

Using the data of Fig. 7 at temperatures of 333, 353, and 373 K in the time interval of 1200-3600 s based on equation (5) k_{ef} was calculated.

The results of the k_{ef} calculation are presented in Table 2.

The effective activation energy was determined using a graphical method (Fig. 8).

The effective activation energy is:

$$E_{ef} = -8.314 \cdot (-2494.4) = 20738 \text{ J/mol} = 20.738 \text{ kJ/mol}$$

In the range of 333-353 K and 353–373 K for polycondensation reactions of RPh with formaldehyde with known values of E_{ef} , k_0 , C_0 , and τ_0 , we obtain equations (9) and (10) of the dependence of the PhFR yield on the temperature and duration of the process:

$$y_{333-353} = 100 - \frac{100}{1.65 + 1.07 \cdot (\tau - 1200) \cdot e^{\frac{-2494.4}{T}}} \quad (9)$$

$$y_{353-373} = 100 - \frac{100}{2.05 + 2.45 \cdot (\tau - 1200) \cdot e^{\frac{-2494.4}{T}}} \quad (10)$$

To confirm the adequacy of the kinetic model, the characteristics of this resin were compared with the predicted characteristics obtained on the basis of the experimental statistical model.¹⁹ The results of the comparison

of the experimental statistical and kinetic models are shown in Table 3.

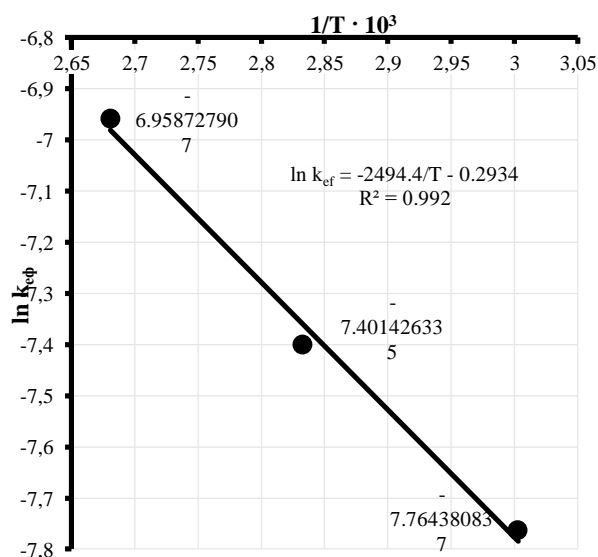


Fig. 8. The effective activation energy identification plot

Table 3. Optimal conditions for the synthesis of PhFR

Process parameters				Response function value			
X_1 (concentration of a catalyst), wt % on RPh	X_2 (mass ratio of RPh to formalin)	X_3 (process temperature), K	X_4 (process duration), min	Y_1 (resin yield), wt % on RPh	Y_1^{reg} , (resin yield), wt % on RPh	Y_2 , (SP of resin), K	Y_2^{reg} , (SP of resin), K
Calculated values according to the equations given in the in the paper ¹⁹							
2.40	1.95	357	42	–	99.0	–	367
Calculated values according to equation (10)							
–	1.95	357	42	–	95.4	–	–
Experimental values							
2.40	1.95	358	42	95.0	–	366	–

Substituting the found optimal conditions ($T = 357$ K and $\tau = 2520$ s) into the kinetic Eq. (10), we obtain that $y_{357} = 80.2$ wt %. Knowing the mass ratio of RPh to formalin, we find the yield of resin on RPh – 95.4 wt % (Table 3). The values of the outputs calculated according to the kinetic Eq. (10) and the equations given in the paper¹⁹ and experimentally established are practically the same (Table 3), which also proves the adequacy of the found equations.

4. Conclusions

The kinetic patterns of the chemical interaction of concentrated phenols obtained from the phenolic fraction of coal tar with formaldehyde in the presence of hydrochloric acid were calculated.

According to the nature of the dependences of resin yield and softening temperature on the duration of the polycondensation process, it was established that the process passes through three main stages:

1) up to 20 min – the beginning of the polycondensation process and the formation of the main amount of resin;

2) 20-60 min – continuation of the growth of the polymer chain (mainly an increase in the softening temperature of the resin);

3) more than 60 min – completion of the process (yield and resin softening temperature remain almost unchanged).

It was established that most polycondensation reactions of concentrated phenols with formaldehyde take place in the second order. The effective activation energy of the polycondensation process in the interval 333-373 K, which is 20.7 kJ/mol, was calculated using a graphic method.

The use of the proposed equation of the kinetic model of the process makes it possible to accurately predict the yield of the obtained resin in the range of 333–373 K. Also, the obtained results are important for the optimization and technological design of this process.

The values of the outputs calculated by kinetic equations, experimental statistical model and experimentally determined values are practically the same, which additionally proves the adequacy of the found equations.

Acknowledgements

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Abbreviations

PhFR – phenol formaldehyde resins;

RPh – raw (concentrated) phenols;

SP – softening point;

WPhF – wide phenolic fraction.

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КІНЕТИЧНА МОДЕЛЬ ПРОЦЕСУ ПОЛІКОНДЕНСАЦІЇ КОНЦЕНТРОВАНИХ ФЕНОЛІВ КАМ'ЯНОВУГІЛЬНОЇ СМОЛИ З ФОРМАЛЬДЕГІДОМ

Анотація. Одержано фенолоформальдегідні смоли методом поліконденсації концентрованих фенолів з формальдегідом у присутності хлоридної кислоти. Концентрування фенолів здійснювали, обробляючи фенольну фракцію кам'яновугільної смоли водним розчином гідроксиду натрію з наступною нейтралізацією водорозчинних фенолятів хлоридною кислотою. Отримано кінетичні залежності виходу смоли та температури розм'якшення від тривалості процесу за 333, 353 та 373 К. Визначено порядок реакції та встановлено ефективну енергію активації цього процесу графічним методом. В інтервалі 333–373 К для реакції поліконденсації отримано рівняння залежності виходу смоли від температури та тривалості процесу.

Ключові слова: фенолоформальдегідні смоли, новолак, хлоридна кислота, кінетика.