



# Effect of molar ratios of phenol, formaldehyde, and catalyst on the properties of phenol–formaldehyde resin with partial replacement of synthetic phenol with depolymerized lignocellulose biomass

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Received: 28 July 2021 / Revised: 18 October 2021 / Accepted: 28 October 2021 / Published online: 18 November 2021  
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## Abstract

This article presents a method for fractionating and separating phenolic compounds from liquid pyrolysis products of lignocellulosic biomass by a three-stage method, in which up to 30% of phenolic compounds can be extracted. The composition of the phenol-substituting fraction was analyzed by the gas chromatography–mass spectrometry (GCMS) method. The isolated phenolic compounds were used in the synthesis of phenol–formaldehyde resins as a phenol-substituting fraction, with the replacement of 40% of the synthetic phenol in the recipe. Various molar ratios of phenol/formaldehyde and phenol/sodium hydroxide in the resin synthesis recipe were considered, as well as their influence on the strength of the adhesive joint and the proportion of free formaldehyde in the finished modified resin. The results of the studies showed that the optimal molar ratio of phenol/formaldehyde is 1:1.98, with a tensile strength of 1.63 MPa and a free formaldehyde fraction of 0.10% in the resin. The phenol/sodium hydroxide molar ratios considered in this paper did not show an optimal molar ratio, but a tendency to reduce the free formaldehyde content in the resin with a decrease in the introduction of an alkaline catalyst into the resin recipe was revealed, while the strength of the adhesive joint remains normal.

**Keywords** Phenol-substituting fraction · Neutral substances · Depolymerization of biomass · Pyrolysis · Free formaldehyde · Phenol · Vegetable phenol · Wood resin

## 1 Introduction

Phenol–formaldehyde resin (PFR) is one of the earliest synthetic polymers sold under the brand name «bakelite». In terms of application, the global phenol–formaldehyde resin market can be divided into varnishes, insulation, molding mixture, wood glue, and others. One of the most important uses of phenol–formaldehyde resin is in the production of composite boards [1, 2].

In industrial practice, there are two main methods for producing phenol–formaldehyde resins. In one method, the excess formaldehyde reacts with phenol in the presence of the main catalyst in an aqueous solution to produce resol. In another method, when an amount of formaldehyde to phenol

less than the equimolar is preserved in an acidic medium, a novolac resin is obtained [3, 4].

Resol can be cured with a solid thermosetting mesh polymer. For example, it can be used between layers of wood veneer and heated under pressure to form plywood. Phenol is a dangerous and carcinogenic substance. Another important factor is the price of synthetic phenol. The cost of phenol most significantly affects the cost of the finished phenol–formaldehyde resin since it is an expensive oil derivative. Oil, in turn, is a non-renewable natural resource, and its reserves are being depleted. In this regard, the search for alternative sources of phenols is relevant [5, 6].

The recent development of macromolecular studies in the lignin-polymer materials systems has shown the great potential of lignin as a raw material source [7]. The phenolic structure of lignin may make it a promising substitute for phenol in the synthesis of phenol–formaldehyde resins. Also, the source of phenol can be lignocellulosic biomass, which is formed in the form of waste in

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woodworking industries. The depolymerization of biomass is carried out by the method of rapid ablation pyrolysis. The main product of this type of processing is pyrolysis liquid [8–11].

The effectiveness of the final wood glue was found to depend on the properties of the lignin: the type of lignin, the source of lignin (coniferous or deciduous wood), the type of pretreatment, and the molecular weight of the lignin. It also depends on the synthesis conditions: the phenol substitution coefficient, the molar ratio of phenol/formaldehyde, the sodium hydroxide loading for the synthesis of resol, the reaction temperature, and the reaction time [12].

All attempts to replace phenol with renewable raw materials lead to changes in the properties of the phenol–formaldehyde resin. In this study, the free formaldehyde indicator was chosen to assess the quality of the resin due to the fact that the release of formaldehyde during the production of plywood is a very important factor in determining the choice of a binder [8, 13–16].

In studies [17–24], various phenolic resins with various phenol substitutes were obtained, but the indicators of free formaldehyde were overestimated.

Improving the quality of modified resins is carried out by various methods; for example, in [17], a study was carried out to improve the mechanical properties by modifying phenol–formaldehyde resole resin using some additives such as boric acid, sulfuric acid, and lignin biomass. In studies [20, 25], the optimal molar ratios in the synthesis of PFR are studied, where lignin and ammonium liginosulfonate of coniferous species were used as a substitute for phenol.

This article studies the effect of the molar ratio of phenol to formaldehyde and phenol to catalyst (NaOH) on the strength and content of free formaldehyde in a modified resin, in which 40% of synthetic phenol was replaced by a phenol-substituting fraction (PSF) obtained by fractionating liquid pyrolysis products of birch sawdust. Substitution of 40% was chosen as the best option from the economic and environmental point of view [26, 27].

## 2 Materials and methods

### 2.1 Properties of the initial raw material

Pyrolysis liquid was obtained from birch chips at the FPP02 fast pyrolysis plant (<https://energolesprom.ru/>). The temperature of the rapid pyrolysis process was  $500 \pm 50^\circ\text{C}$ . The permissible size of the wood chips is not more than 20 mm (thickness) and 10 mm (length). The wood chips were pre-dried to the humidity of no more than 15%. The output of the products on the FPP02 unit is shown in Table 1.

**Table 1** Material balance of the birch chip pyrolysis process at the FPP02 plant

Product	Yield, weight
Char	22%
Liquid products	56%
Gas	22%

### 2.2 Isolation of phenolic compounds from the pyrolysis liquid

The concentration of phenolic compounds in the pyrolysis liquid includes three stages. In the first stage, water, volatile compounds, and acetic acid are separated from the pyrolysis liquid. This process was carried out by vacuum distillation at a temperature of  $80^\circ\text{C}$ , a residual pressure of 0.1–0.2 atm, and a mixing speed of 45 rpm on a rotary evaporator (RV 10 digital V, company ICA). The second stage involves the removal of carbohydrate components and other water-soluble compounds. For this purpose, water extraction of the pyrolysis liquid was carried out. The pyrolysis liquid, freed from acids, was mixed with hot water in a ratio of 1:1. The mixture was settled in a dividing funnel, and then the mixture was separated to obtain the upper and lower fractions. Furthermore, the lower fraction was treated with a solvent, n-hexane, to extract the neutral compounds. Neutral compounds include substances that represent a class of esters or aromatic substances and that, as the practice has shown, do not participate in the synthesis process and negatively affect the quality of the finished resin [28–30]. In the process of this treatment, a PSF is obtained with a content of about 30% of phenol and its derivatives, which was used in the synthesis.

The material balance of the concentrating phenolic compounds was calculated. The data is presented schematically in Fig. 1. Side cuts from separation can be of value in the market. For example, the condensate formed during the distillation process is a source of wood vinegar, which is used in agriculture and the national economy. Research is also underway to use the dried carbohydrate fraction as a polyol component in the production of polyurethane foams [29].

It is worth noting that the water and organic solvents released during the release of phenols from the pyrolysis liquid can be recovered. This is important from the point of view of the reagent economy and environmental aspects. The residues formed during the recovery process can be burned in order to obtain energy.

The chemical composition of the samples was determined using gas chromatography–mass spectrometry (GSMS). GCMS was carried out on a GCMS-QP2010 device (Shimadzu Company) on an HP-5MS column (30 m

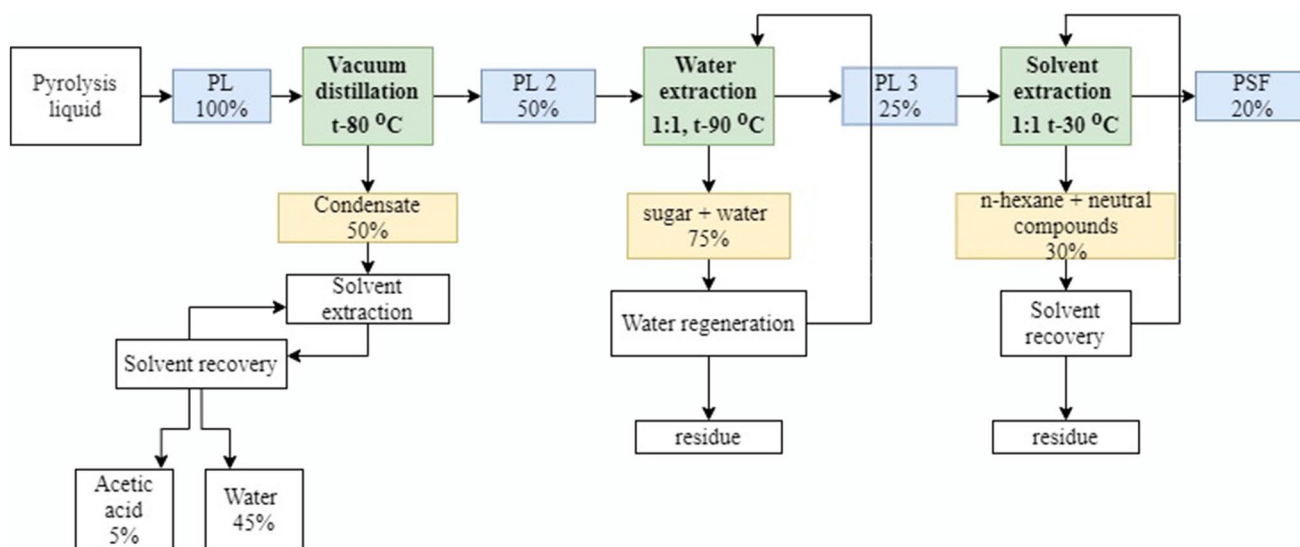


Fig. 1 Scheme of separation of pyrolysis liquid for obtaining a PSF

length, 0.320 mm diameter, and 0.25 um film thickness) using the following parameters: helium grade A as the carrier gas, injector temperature of 300°C, flow rate of 1 ml/min through the column, mode with flow division, division in the ratio 1:50, 3 ml/min purge, and temperature program of the thermostat – 80°C for 2 min, gradient increase to 200°C at a speed of 10°C/min, and then hold at 200°C for 6 min. The mass spectrometer parameters were as follows: the temperature of the ion source is 270°C, scan mode; the range of recorded ions is 35–600 m/z; and the solvent deduction time is 2 min. The sample was taken using a Gilson precision syringe in the amount of 1 mL.

### 2.3 Synthesis of modified phenol–formaldehyde resin

The synthesis was carried out in a 500 mL flask equipped with a reverse refrigerator, a thermometer, and a mixer. At room temperature, PSF, phenol, water, the first portion of the catalyst, and formalin were loaded into the reactor.

Based on the standard recipe of phenol–formaldehyde resin, a recipe was previously developed with a 40% substitution of synthetic phenol with a phenolic fraction obtained from liquid wood pyrolysis products. The recipe is presented in Table 2.

Then, the mixture was heated to a temperature of 45–65°C and kept for 105 min. After aging, the mixture was boiled for 15 min. After that, the mixture was cooled to a temperature of 70–72°C for the introduction of a second portion of the catalyst. Then, the mixture was kept for 15 min at a temperature of 67–69°C after careful mixing. After the synthesis was completed, the resin was cooled.

Table 2 Basic recipe for modified PFR

Component	Concentration	Yield, weight
PSF	100%	10.14%
Phenol	100%	14.90%
Formalin	37%	51.20%
Sodium hydroxide (water solution)	43%	18.21%
Water	100%	5.55%

Table 3 The ratio of formaldehyde and catalyst to phenol in the main recipe

Phenol/formaldehyde	1/2.38
Phenol/sodium hydroxide	1/0.73

### 2.4 Determining the molar ratio of the components of the main recipe

Based on the standard recipe for PFR, a recipe was previously developed with a 40% substitution of synthetic phenol with a phenolic fraction obtained from liquid wood pyrolysis products (Table 2).

To determine the molar ratio, it was assumed that the PSF is considered to be pure phenol. Under this assumption, the masses of phenol and PSF are added together to calculate the amount of phenol in the recipe. Thus, all the ratios of formalin and sodium hydroxide presented in the article are given in relation to the total phenol (Table 3).

At this ratio of components, the experimental PFR has a strength value of 2.61 MPa and a free formaldehyde

value of 2.83%. The strength of this resin corresponds to the required values, but the value of free formaldehyde is much higher than the norm.

Based on this, syntheses were carried out with a change in the molar ratios of phenol to formaldehyde and phenol to sodium hydroxide, which would reduce the value of the proportion of free formaldehyde in the resin while maintaining the strength readings within the required limits. It should also be taken into account that with a decrease in the formaldehyde content in the resin, the strength of the adhesive joint also decreases. Therefore, the optimal molar ratio of phenol, formaldehyde, and sodium hydroxide needs to be chosen in the synthesis so that the strength value is sufficient. According to GOST (Russian National Standard) 20,907–2016 “Liquid phenol formaldehyde resins specifications,” this value for the SFZh-3014 grade is 1.47 MPa.

To assess the effect of the ratio of components, an experimental resin was obtained according to the main formulation. To evaluate the effect of formaldehyde on the properties of the PFR, four additional resins were obtained that differed in the molar ratio of phenol to formalin in the recipe (Table 4).

To evaluate the effect of the catalyst loading, three more resins were obtained that differed in the molar ratio of phenol to sodium hydroxide from the main recipe. The ratios are shown in Table 5.

## 2.5 Methods of sample analysis

The proportion of free formaldehyde in the resin was determined by method 1, as specified in GOST 16,704–71 (Russian National Standard). First, the pH of the control sample on the water is determined. To do this, distilled water was brought to a pH of 3.5, and then a solution of hydroxylamine hydrochloride was added. After 10 min, the pH of the control sample was measured. Next, the readings are determined in the working solution. To do this, the resin suspension is dissolved in distilled water, and with continuous stirring, the solution is brought to a pH of 3.5, after which 10 mL of hydroxylamine hydrochloride solution is added. After 10 min, the main sample is titrated with a solution of

**Table 4** Molar ratios for evaluating the effect of formaldehyde on resin properties

№	Phenol	Formaldehyde
1	1	1.60
2	1	1.79
3	1	1.98
4	1	2.17

**Table 5** Molar ratios for evaluating the effect of the catalyst on resin properties

№	Phenol	Sodium hydroxide
1	1	0.82
2	1	0.67
3	1	0.65

sodium hydroxide with a concentration of 0.1 N to the pH value of the control sample.

The mass fraction of free formaldehyde in resin b was calculated by the following formula:

$$X = \frac{V * 0.003 * 100}{m}, \%$$

where  $V$  is the volume of sodium hydroxide solution used for titration, 0.003 is the mass of formaldehyde that corresponds to 1 cm<sup>3</sup> of sodium hydroxide solution, and  $m$  is the resin weight in grams.

## 2.6 Bonding and determination of the sample strength

Birch veneer sheets (12 cm × 12 cm) were used for bonding. Bonding was carried out according to GOST 20,907–75 (Russian National Standard) and according to clause 4.15 on the NORDBERG ECO N3620L hydraulic press, which is equipped with heating plates. The mode parameters of bonding are shown in Table 6.

Next, four samples were cut out of each sheet of three-layer plywood in accordance with GOST 9620–72 (Russian National Standard). Before breaking, the samples were kept in a bath of boiling water for 1 h. After boiling, the samples were kept at room temperature for 10 min. Furthermore, the samples were torn on a universal electromechanical testing machine.

**Table 6** Parameters for gluing samples

Parameter	Value
Bonding area	144 cm <sup>2</sup>
Consumption	0.014 g/cm <sup>2</sup>
Temperature	126–130°C
Pressure	1.96–2.45 MPa (20–25 kgf/cm <sup>2</sup> )
Press exposure time	7 min

### 3 Results and discussion

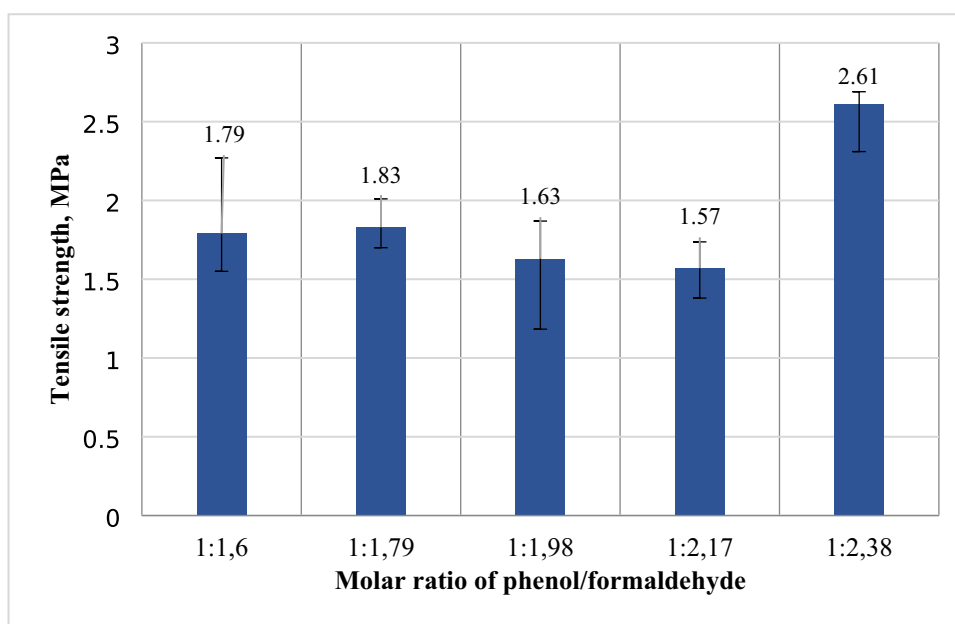
#### 3.1 Analysis of the chemical composition of the PSF

The analysis of the phenol-substituting fraction by GCMS showed the presence of substances belonging to the class of phenols, with a content of up to 30%. Pure phenol was identified as well as its substituted homologs, which are represented in the form of creosol (5.32%), eugenol (1.64%), and apocenin (0.66%). In addition to phenols, there are compounds that are present at a significant percentage. These are compounds that represent the class of ketones (4.58%) and aldehydes (2.71%). The analysis also showed the presence of acids up to 3.44%, which are most represented by acetic acid, the content of which is 2.67%. Acids can be inhibitors in the PFR synthesis process and, as a result, may require an increase in the amount of alkaline catalyst. This problem

**Table 7** Composition of the PSF

Types	%
Acid	3.44
Alkane	0.18
Aromatic compounds	1.29
Alcohols	0.56
Aldehydes	2.71
Alkenes	1.44
Ketone	4.58
Phenol	29.64
Carbohydrates	0.13
Not identified	56.01

**Fig. 2** Graph of the dependence of the strength of the adhesive joint on the molar ratio of phenol/formaldehyde



can be solved by carrying out a better vacuum distillation process in the preparation of the PSF for the synthesis. The full composition of the phenol-substituting fraction is presented in Table 7. The pyrolysis liquid has a complex multicomponent composition. Therefore, a large percentage of unidentified substances stay in the analysis, among which there is a possibility that representatives of the phenol class are contained.

#### 3.2 Effect of the molar ratio of phenol to formaldehyde on the strength and percentage of free formaldehyde in the resin

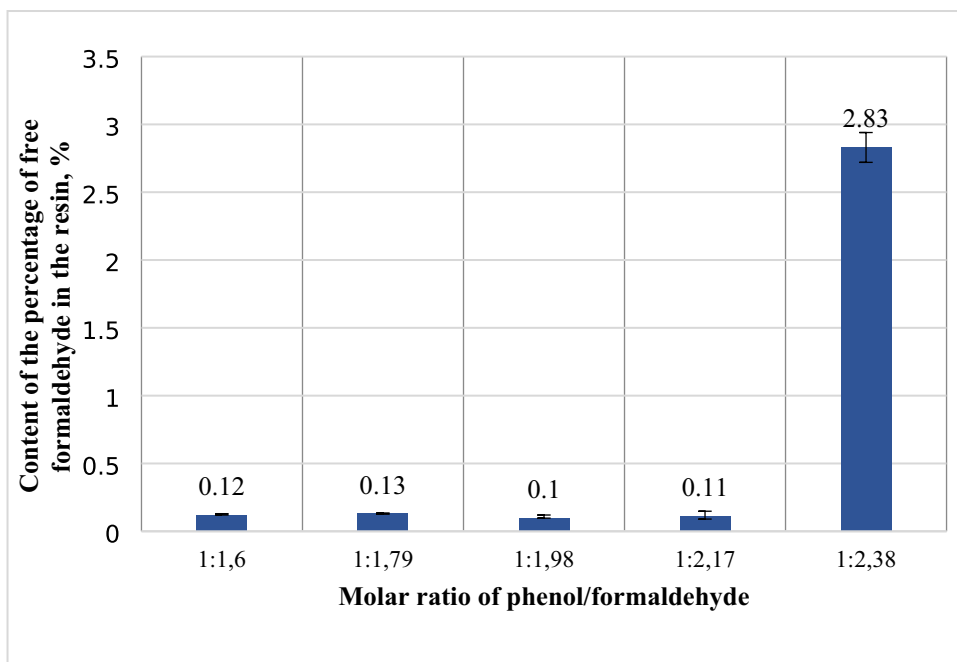
Figure 2 shows a graph of the strength of the adhesive joint of samples that are glued with experimental resins. For the bonding of the samples, a resin was used, which was obtained according to the main recipe, and four resins were also used, in which the molar ratio of phenol/formaldehyde was changed.

At any given ratio of phenol to formaldehyde, the strength of the adhesive joint meets the requirements of GOST 20,907–2016 (Russian National Standard) (the norm is not less than 1.47 MPa). The maximum value, which is 2.61 MPa, is achieved with a 1:2.38 molar ratio of phenol/formaldehyde (basic recipe). At a molar ratio of 1:2.17, the strength of the adhesive joint has the lowest value among all the studied molar ratios, which is equal to 1.57 MPa.

An important indicator for the phenol–formaldehyde resin is also the percentage of free formaldehyde. This indicator was determined for experimental resins. Figure 3 shows a graph of the dependence of the percentage of free



**Fig. 3** Graph of the dependence of the percentage of free formaldehyde on the molar ratio of phenol/formaldehyde



formaldehyde in the resin on the molar ratio of phenol to formaldehyde.

According to the presented data, it can be seen that with a molar ratio of phenol/formaldehyde of 1:2.38 (the basic recipe), the resulting resin has a critically high value of the percentage free formaldehyde, which significantly exceeds the allowable values according to GOST 20,907–2016 (Russian National Standard) (the norm is not more than 0.10%). Most probably, this factor is the reason for the high strength values. Experimental resins obtained at other molar ratios have much lower free formaldehyde values. When comparing the percentage of free formaldehyde for the ratios of 1:2.17 and 1:2.38, a sharp increase is observed. This may indicate that formalin is in excess compared to synthetic phenol. It is assumed that in this range, all the phenol present in the mixture reacts with formaldehyde, and with a further increase in the amount of formaldehyde, it remains unbound. According to experimental data, the optimal ratio of phenol to formaldehyde in a resin with a phenol-substituting fraction is 1:1.98. At this ratio, the percentage of free formaldehyde in the resin is 0.1%, and the strength is 1.63 MPa. This data meets the standards.

The experimental resins obtained at a molar ratio of 1:1.6 phenol/formaldehyde have a free formaldehyde value of 0.12%; at a ratio of 1:1.79, the free formaldehyde value is 0.13%; and at a ratio of 1:2.17, the percentage of free formaldehyde is 0.11%. To choose the optimal molar ratio of phenol to formaldehyde, it is necessary to take into account both the strength values and the percentage of free formaldehyde.

### 3.3 Effect of the molar ratio of phenol to sodium hydroxide on the strength and proportion of free formaldehyde

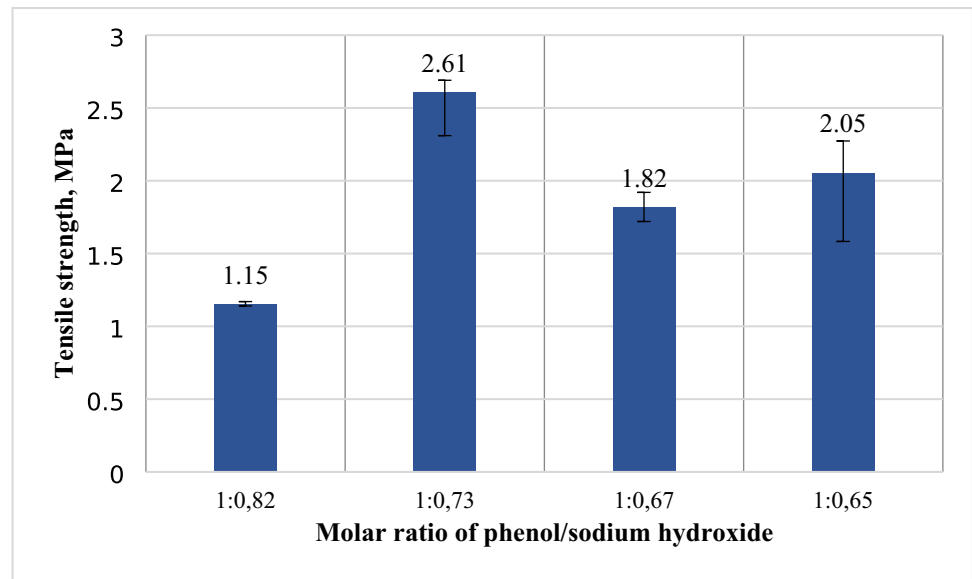
Figure 4 shows a graph of the strength of the adhesive joint of samples glued with the modified PFR obtained with a different ratio of phenol and alkaline catalyst. In the main recipe, the ratio of phenol to alkali is 1:0.73.

The maximum strength value (2.61 MPa) is the resin obtained according to the main recipe (1:0.73). With a ratio of 1:0.67 and 1:0.65, the resin has a strength of 1.82 MPa and 2.05 MPa, respectively, which meet the requirements of GOST 20,907–2016 (Russian National Standard). The resin with a ratio of 1:0.82 has a minimum strength value (1.15 MPa) and does not meet the norm (1.47 MPa).

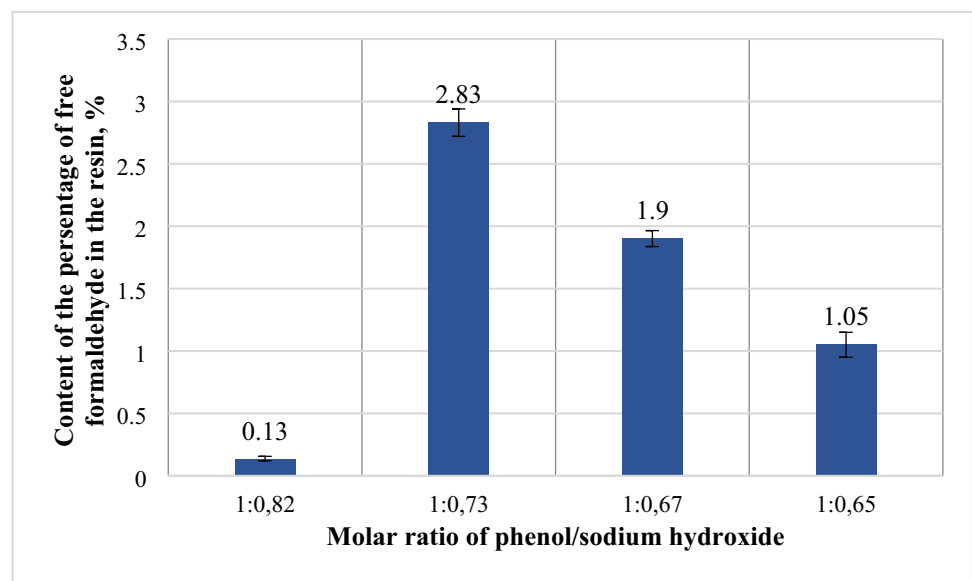
The percentage of free formaldehyde was also determined for these resins. The data is shown in Fig. 5.

As mentioned earlier, the resin with a molar ratio of 1:0.73 (the main recipe) has a percentage of free formaldehyde that does not correspond to the norm. When comparing this value, it is worth noting that it remained the highest both when increasing and decreasing the amount of catalyst in the recipe. A noticeable decrease in the free formaldehyde to 0.13% can be noted, which occurs with a slight increase in the catalyst concentration (ratio 1: 0.82). This result most likely suggests that in the synthesis of PFR according to the main recipe at a phenol/formaldehyde molar ratio of 1: 2.38, there is a lack of catalyst, due to which a slow reaction and incomplete binding of the synthesis components: Phenol and formaldehyde occur, which gives high values of the free formaldehyde. But even if an increase in catalyst affects the

**Fig. 4** Graph of the strength of the adhesive joint of samples glued with the modified PFR as a function of the molar ratio of phenol/sodium hydroxide



**Fig. 5** Graph of the dependence of the percentage of free formaldehyde on the molar ratio of phenol/sodium hydroxide



binding of phenol to formaldehyde and decreases the free formaldehyde value, this increase in the recipe significantly affects the strength index, which decreases to 1.15 MPa (Fig. 4). This conclusion can be explained by the fact that an increase in the alkaline catalyst affects the water resistance of the glue line and decreases its strength.

Two other resins with ratios of 1:0.67 and 1:0.65 that have the proportion of free formaldehyde equal to 1.9% and 1.05%, respectively, do not meet the norm value. However, it should be noted that at these values, there is a tendency to reduce the percentage of free formaldehyde, while the strength of the adhesive joint remains within the normal range.

According to the presented data, there is no direct relationship between the molar ratio of phenol/sodium hydroxide

and the percentage of free formaldehyde. There are optimal values that should be followed to maintain the strength indicators at the required level.

In addition, in the future, in order to maximize the effect on the percentage of free formaldehyde, it is necessary to change the ratio of phenol/sodium hydroxide and phenol/formaldehyde simultaneously.

## 4 Conclusion

Comparing the tensile strength (MPa) and the percentage of free formaldehyde (%), and following the standards specified in GOST 20,907–2016 (Russian National Standard), the optimal molar ratio of phenol/formaldehyde in the recipe

for the synthesis of a modified phenol–formaldehyde resin with a strength value of 1.63 MPa and a percentage of free formaldehyde of 0.10% is 1:1.98.

Within the limits of the phenol/formaldehyde ratio from 1:1.6 to 1:2.17, the effect of formaldehyde on the strength and percentage of free formaldehyde is not significant. However, with an increase in the amount of formaldehyde in the recipe, the indicators increase significantly. It is assumed that with an increase in the percentage of free formaldehyde in the resin, its strength indicators also increase.

The molar ratios of phenol/sodium hydroxide considered in this paper (1:0.82; 1:0.73; 1:0.67; 1:0.65) did not show an optimal molar ratio and need further study. To select the optimal value of the phenol/sodium hydroxide ratio, it is necessary to study the effect of the catalyst loading on the synthesis of the PFR according to the recipe, which was chosen in this paper as the optimal ratio of phenol/formaldehyde (1:1.98). To maximize the effect on the percentage of free formaldehyde, it is necessary to simultaneously change the ratio of phenol/sodium hydroxide and phenol/formaldehyde.

Also, a molar ratio of phenol/sodium hydroxide lower than 1:0.65 should be considered since there is a tendency to reduce the content of the proportion of free formaldehyde in the resin with a decrease in the introduction of an alkaline catalyst into the resin recipe, while the strength of the adhesive joint remains normal. Also, one can consider the option of a longer synthesis since there is an assumption that the synthesis with substituted phenols takes longer than with synthetic ones.

**Funding** This study was funded by Kazan National Research Technological University and EnergoLesProm LLC.

## Declarations

**Conflict of interest** The authors have no relevant financial or non-financial interests to disclose. The authors have no conflicts of interest to declare that are relevant to the content of this article. All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript. The authors have no financial or proprietary interests in any material discussed in this article.

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