Environmental Engineering and Management Journal *April 2018, Vol.17, No. 4, 771-781*
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

MATHEMATICAL MODELLING FOR PHENOLATION OF SPENT SULFITE LIQUOR

Andrei Ionuţ Simion[1], Cristina-Gabriela Grigoraș[1], Alexandru Chiriac[2], Cătălin Nicolae Tâmpu[3], Lucian Gavrilă[1]*

[1] *"Vasile Alecsandri" University of Bacău, Faculty of Engineering, Department of Chemical and Food Engineering, 157 Calea Mărăşeşti, 600115 Bacău, Romania*
[2] *"Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Mangeron Blvd, 700050 Iasi, Romania*
[3] *"Vasile Alecsandri" University of Bacău, Faculty of Engineering, Department of Engineering and Management, Mechatronics, 157 Calea Mărăşeşti, 600115 Bacău, Romania*

Abstract

In this study major factors affecting the phenolation process of lignosulfonate (LS) waste liquor (recovered from pulp and paper industry) were optimized in order to improve LS substitution for replacing petroleum-based phenols during phenolic resin manufacturing. Four different parameters, namely phenol/lignosulfonate ratio, time, temperature and lignosulfonate waste liquor concentration, were varied in an experimental program having as response function the reaction yield. Response Surface Methodology (based on central composite or Box-Behnken designs) and Artificial Neuronal Network were applied for establishing the process parameters impact on phenolation yield.
The developed mathematical models presented a high accuracy being able to adequately estimate the phenol conversion and adduct formation. Yields over 80 % were obtained when lignosulfonate waste liquor with a concentration in lignosulfonate between 35 % and 45 % was used in a ratio of 1:1 with phenol and the reaction was conducted at temperatures in a range of 100 °C – 110 °C for a period of time of 3.0 – 3.5 hours.

Key words: Artificial Neural Network, lignosulfonate, mathematical optimization, resin, Response Surface Methodology

Received: May, 2017; Revised final: January, 2018; Accepted: March, 2018; Published in final edited form: April 2018

1. Introduction

Phenolic resins, known as the first polymer synthetized at industrial level, are thermosetting resins that form a three-dimensional network structure through covalent bonds (Shudo et al., 2017). Characterized as possessing high aromatic density, very good thermal, chemical and mechanical stability and strength, high thermal insulating properties (Martin et al., 2006), and solvent resistance (Foyer et al., 2016), they are widely used in the aerospace, automotive, construction, and semiconductor industries (Shudo et al., 2016). These types of resins are successfully employed to fabricate a large variety of products from electric laminates to carbon foams (Zhao et al., 2009), adhesives (Roslan et al., 2014; Yang and Frazier, 2016), molding compounds (Hirano and Asami, 2013), acid-resistant coatings (Biedermann and Grob, 2006a, 2006b), fiber-reinforced composites (Bu et al., 2014; Li et al., 2016; Wu et al., 2017) and binders (Wang et al., 2017).

There are two types of phenolic resins commonly resulting from a synthesis process using two reagents: phenol and formaldehyde. When an

* Author to whom all correspondence should be addressed: e-mail: lgavrila@ub.ro; Phone: +40 234 524 411 ext. 145; Fax: +40 234 580 170

excess of formaldehyde and an alkaline catalyst are used *resol phenolic resin* is obtained while an excess of phenol and acidic *p*H conditions lead to *novolac phenolic resin* (Foyer et al., 2016; Noparvar-Qarebagh, 2016). In the last period, the rising cost and the predictable upcoming insufficiency of petrochemicals have stimulated the necessity to evaluate the possibility of replacing the phenol with other products (Greco et al., 2016). Dedicated researches conducted to the conclusion that lignosulfonates (compounds from pulp and paper wastewaters known as chemically stable, resistant to biological degradation, and difficult to separate by conventional wastewater treatment methods (Zulfikar et al., 2012)) constitute one of the best alternatives (Hu et al., 2012; Perez et al., 2007). Even though good results were reported when non-modified lignosulfonates were incorporated in phenolic resin, their reactivity is improved if the chemical structure is modified (Alonso et al., 2001), one way to accomplish this structure change being represented by the phenolation reaction. According to data reported by Alonso et al. (2005) and by Hu et al. (2011), the mentioned method involves: benzyl-hydroxyl group protonation; dehydration at the α-carbon in order to give a carbonium ion; electrophilic attack by carbonium ion of the phenol molecule leading to a phenol condensation product; incorporation of *ortho* or *para*-phenyl substituent to the α-hydroxyl groups of the propane side chains and adduct fragmentation and insures, in the same time, a decrease of molecular weight supporting a more appropriate incorporation of phenolation products to phenolic resins.

Considering the information previously presented, this paper is focused on the optimization of the main factors affecting the lignosulfonate phenolation process. To this purpose, lignosulphonate (LS) from spent sulphite liquor resulting from pulp and paper industry and phenol (P) were used and four different parameters: P/LS ratio, time, temperature and LS concentration were varied in an experimental program having as response function the reaction yield. In order to obtain the optimal values for the above-mentioned parameters two different methodologies were employed: Response Surface Methodology (RSM) and Artificial Neural Network (ANN).

RSM is a widely used collection of mathematical and statistical techniques which gives, among others, a second order polynomial equation able to accurately describe the experimental data behavior (Xiang et al., 2015). It applies for response functions influenced by different variables (Koricic et al., 2016) and has as main aim to simultaneously optimize the levels of these variables in order to achieve the best results (Almeida Bezerra et al., 2008; Shirneshan et al., 2016). In the present study, two second-order symmetrical RSM designs were developed: central composite design (CCD) and Box-Behnken design (BBD) the difference between them being given by the selection of experimental points and the number of runs. ANN is an assembly of simple computational units interlinked by a system of connections (Cheng and Titterington, 1994) which implement algorithms that attempt to achieve a neurological related performance including learning and making generalization from similar situations (Cemek et al., 2013; Meireles et al., 2003; Rajakovic-Ognjanovic et al., 2014).

The simplest ANN requires three layers (input, hidden and output), activation function, learning technique and weights. In terms of layers, the input one receives information and passes it for processing; the hidden layer processes the information offered by the input layer while the output layer receives processed information from hidden layers and give the results. The activation function affects the neural network behavior and scales the output into an adequate range. The learning system adapts itself to various changes insuring that during the training phase weights can be modified in response to input/output chances (Dharwal and Kaur, 2016). For this paper, the experimental acquired data were used to build and train an artificial neural network in order to decide if it is more appropriate than RSM for establishing the optimal values for the parameters affecting the LS phenolation reaction.

The accuracy of the resulted mathematical models was investigated by applying several different tests: sequential model sum of squares, lack of fit test and Analysis of Variance (ANOVA) test.

2. Material and methods

2.1. Reagents

Phenol used for the experiments was of analytical purity and was purchased from Sigma Aldrich (Redox Lab Supplies Bucharest, Romania). Lignosulfonate waste liquor (with 50 wt % LS) was obtained from a local pulp and paper industry. All the solutions were prepared only with demineralized water.

2.2. Phenolation reaction

Following the experimental setup detailed in Table 1, Table 2 and in Table 3 from the section dedicated to RSM modelling, different proportions of lignosulfonate waste liquor of different concentrations and 50 g of pure phenol were solubilized in 500 mL of demineralized water and introduced in a 1 L glass laboratory reactor equipped with a thermometer and a reflux condenser. Sulphuric acid (0.5 wt % reported at the phenol quantity) was added in order to insure an acidic media.

The resulted mixtures were heated under stirring on a Nahita Blue 692 magnetic heating plate (Auxilab, Spain) to various temperatures for different periods of time according to the established exploratory plan. At the end, the remaining water was removed by atmospheric pressure distillation.

Table 1. Independent variable and levels used for CCD and BBD

Parameter	***Levels of variation***	
	CCD	***BBD***
A (P/LS ratio)	0.5; 1; 1.5; 2; 2.5	1; 1.5; 2
B (time, hours)	2; 2.5; 3; 3.5; 4	2.5; 3; 3.5
C (Temperature, °C)	80; 90; 100; 110; 120	90; 100; 110
D (LS concentration, %)	35; 40; 45; 50	35; 40; 45

Table 2. CCD exploratory plan for LS phenolation reaction

Run	***A P/LS ratio***	***B Time, t [hours]***	***C Temperature, T [˚C]***	***D Concentration, LS [%]***	***Yield, η [%]***		
					1st trial	***2nd trial***	***3rd trial***
1	1	2.5	90	35	68.80	67.29	67.63
2	2	2.5	90	35	22.11	21.42	22.49
3	1	3.5	90	35	69.03	71.17	67.93
4	2	3.5	90	35	38.33	41.05	37.87
5	1	2.5	110	35	83.71	82.71	82.20
6	2	2.5	110	35	42.15	43.67	41.01
7	1	3.5	110	35	86.02	86.88	85.85
8	2	3.5	110	35	44.32	46.71	44.19
9	1	2.5	90	45	67.60	67.40	66.79
10	2	2.5	90	45	21.22	20.99	21.45
11	1	3.5	90	45	68.87	68.04	70.04
12	2	3.5	90	45	31.30	31.99	31.27
13	1	2.5	110	45	78.89	76.44	80.63
14	2	2.5	110	45	45.70	45.20	44.92
15	1	3.5	110	45	86.10	82.48	86.87
16	2	3.5	110	45	47.50	46.55	46.98
17	0.5	3	100	40	85.52	86.97	84.92
18	2.5	3	100	40	26.53	26.98	26.34
19	1.5	2	100	40	43.21	43.51	43.12
20	1.5	4	100	40	52.30	51.10	52.09
21	1.5	3	80	40	40.87	40.01	40.34
22	1.5	3	120	40	59.11	57.45	59.88
23	1.5	3	100	30	58.25	56.85	58.54
24	1.5	3	100	50	60.65	58.77	60.95
25	1.5	3	100	40	54.30	54.73	54.46
26	1.5	3	100	40	55.44	55.83	55.50
27	1.5	3	100	40	54.20	53.66	54.04
28	1.5	3	100	40	52.98	54.20	52.77
29	1.5	3	100	40	53.93	53.66	53.66
30	1.5	3	100	40	56.10	56.44	56.83
31	1.5	3	100	40	53.77	54.09	54.36

2.3. Free phenol determination

A Varian 3400 gas chromatograph (Varian, Inc. USA) with flame ionization detector and helium as carrier gas and equipped with an HP-INNOWax capillary column (0.2 μm thickness, 50 m length, 0.2 mm internal diameter) was used for free phenol determination from every reaction. The method described by Alonso et al. (2005) was followed.

2.4. Reaction yield calculation

The phenolation reaction yield was established as ratio between the amount of phenol registered at the end of reaction and that introduced in the reactor and the results were expressed as percentages.

2.5. RSM modelling

Two different RSM designs (central composite design (CCD) and Box-Behnken design (BBD)), chosen due to the fact that they require a reduced number of experiments, were evaluated with Design-Expert 7.0 software in order to describe linear, quadratic, and interactions occurring in the mathematical model developed on an exploratory plan including various levels of variation for four different parameters considered as affecting the lignosulfonate phenolation reaction. The variation of these factors is given in Table 1.

The quadratic model for predicting the optimal values for the studied parameters is shown by the Eq. (1):

$$Y = A_0 + \sum_{i=1}^{4} A_i X_i + \sum_{i=1}^{4} A_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} A_{ij} X_i X_j \quad (1)$$

where Y is the response function (phenolation reaction yield), A_i, A_{ii} and A_{ij} (i≠j) are the regression coefficients of variables for the linear, quadratic and interaction terms, X_i is a code for the four parameters (A, B, C, D) and X_j is a code for the combinations of the parameters (AB, AC, AD, BC, BD, CD).

2.6. ANN modelling

Data used for RSM development were considered as input and output data for a three-layered feed forward momentum ANN. A varying number of neurons (2 – 8) in the hidden layer was tested with NeuroSolutions 6.0 software. Four input nodes, 2 – 8 hidden neurons, one output node, 3000 epochs, and momentum learning rule were employed for ANN training.

3. Results and discussion

3.1. RSM modelling

Table 2 and Table 3 show the runs for CCD and BDD respectively along with reaction yields registered for each of them. All the experiments were conducted in triplicate

Table 3. BBD exploratory plan for LS phenolation reaction

Run	*A P/LS ratio*	*B Time, τ [hours]*	*C Temperature, t [°C]*	*D Concentration, LS [%]*	*Yield, η [%]*		
					1st trial	*2nd trial*	*3rd trial*
1	2	2.5	100	40	38.50	38.73	38.92
2	2	3	90	40	31.29	30.95	30.88
3	1	3	100	35	81.60	80.46	82.17
4	1	3	90	40	66.12	64.33	65.72
5	2	3	100	35	41.56	41.73	41.77
6	1.5	3.5	100	35	57.67	56.57	58.59
7	1	2.5	100	40	78.33	80.05	78.02
8	1	3	110	40	86.09	87.55	85.92
9	1.5	3.5	110	40	61.33	62.13	61.23
10	1.5	3	110	45	60.11	61.01	59.99
11	1.5	3.5	90	40	47.53	48.05	47.01
12	1	3.5	100	40	83.12	82.46	82.46
13	1.5	3	90	35	44.12	44.83	43.72
14	1.5	2.5	100	45	53.53	54.39	53.16
15	1.5	2.5	110	40	61.02	62.00	61.08
16	1	3	100	45	81.81	82.71	80.42
17	1.5	3	100	40	55.70	55.64	55.09
18	1.5	3	100	40	56.10	55.71	55.09
19	1.5	2.5	100	35	53.40	53.13	52.65
20	1.5	3	110	35	58.21	58.44	57.69
21	1.5	3.5	100	45	57.78	57.95	57.90
22	1.5	2.5	90	40	28.11	27.52	27.60
23	2	3	110	40	33.96	33.38	33.59
24	2	3	100	45	27.33	26.81	27.25
25	2	3.5	100	40	30.14	29.84	30.05
26	1.5	3	100	40	55.44	54.89	55.38
27	1.5	3	100	40	52.98	52.56	52.93
28	1.5	3	90	45	26.18	26.22	25.84
29	1.5	3	100	40	53.77	53.55	52.86

The CCD and BBD developed mathematical models are expressed by Eqs. (2) and (3) given below:

$$Y_{CCD} = 54.49 - 18.10 \cdot A + 2.48 \cdot B + 7.65 \cdot C - 0.10 \cdot D + 1.20 \cdot A \cdot B + 0.39 \cdot A \cdot C + 0.31 \cdot A \cdot D - \\ - 0.89 \cdot B \cdot C - 0.04 \cdot B \cdot D + 0.70 \cdot C \cdot D + 0.68 \cdot A^2 - 1.38 \cdot B^2 + 0.42 \cdot C^2 + 1.54 \cdot D^2 \quad (2)$$

$$Y_{BBD} = 54.49 + 54.60 \cdot A - 22.86 \cdot B + 2.06 \cdot C + 9.78 \cdot D - 2.48 \cdot A \cdot B - 3.29 \cdot A \cdot C - 4.32 \cdot A \cdot D \\ - 3.61 \cdot B \cdot C - 4.78 \cdot B \cdot D - 0.005 \cdot C \cdot D + 4.96 \cdot A^2 + 3.98 \cdot B^2 + 0.31 \cdot C^2 - 5.49 \cdot D^2 \quad (3)$$

The adequacy of the second order polynomial equations obtained by RSM modelling was tested by the mean of various tests: standard deviation (SD) which quantifies data dispersion; sum of squares (SS) and mean of square (MS) which measures the deviation from the mean value; correlation coefficient (R^2) which considers in the same time linear, quadratic and interaction effects; the adjusted coefficient of determination (adj. R^2) which estimates only square and interaction effects between two input variables; the predicted coefficient of determination (pred. R^2) which studies the effects for software generated values; the predicted residual sum of squares (PRESS) which measures the fit of a model to observations samples not involved in model assessment; degrees of freedom (*df*) which reveals the number of values that may vary independently; *F* value and *p* value which show the probabilities of predicting results similar to the experimental data when the null hypothesis is true; lack of fit test and pure error which illustrate the differences between the mathematical model and the experimental data.

The analysis of these tests results (Table 4 and Table 5) reveals that the mathematical models developed by RSM describe accurately the behavior of data recorded for LS phenolation reaction yield. For both of them, R^2, adj. R^2, Pred. R^2 presented values higher than 0.97, 0.94 and 0.84 respectively.

The significance of coefficients found for the two RSM established second order polynomial equations indicate that the more important parameters affecting the LS phenolation process are represented by the P/LS ratio and temperature (p value < 0.0001) and that the time and LS concentration have a lower influence. The interactions between the factors do not affect the reaction yield in a considerable manner.

The "Lack of Fit" results sustain also the RSM models accuracy since the chances that the large values registered for this test could occur due to noise are under 1 %.

Fig. 1 and Fig. 2 depict the response surfaces for reaction yield of the first CCD and of the first BBD sets of runs. Since, according to data given in Table 3 and in Table 4, values recorded for the second and the third set of runs both for CCD and BBD present a high similarity, they were not pictured here.

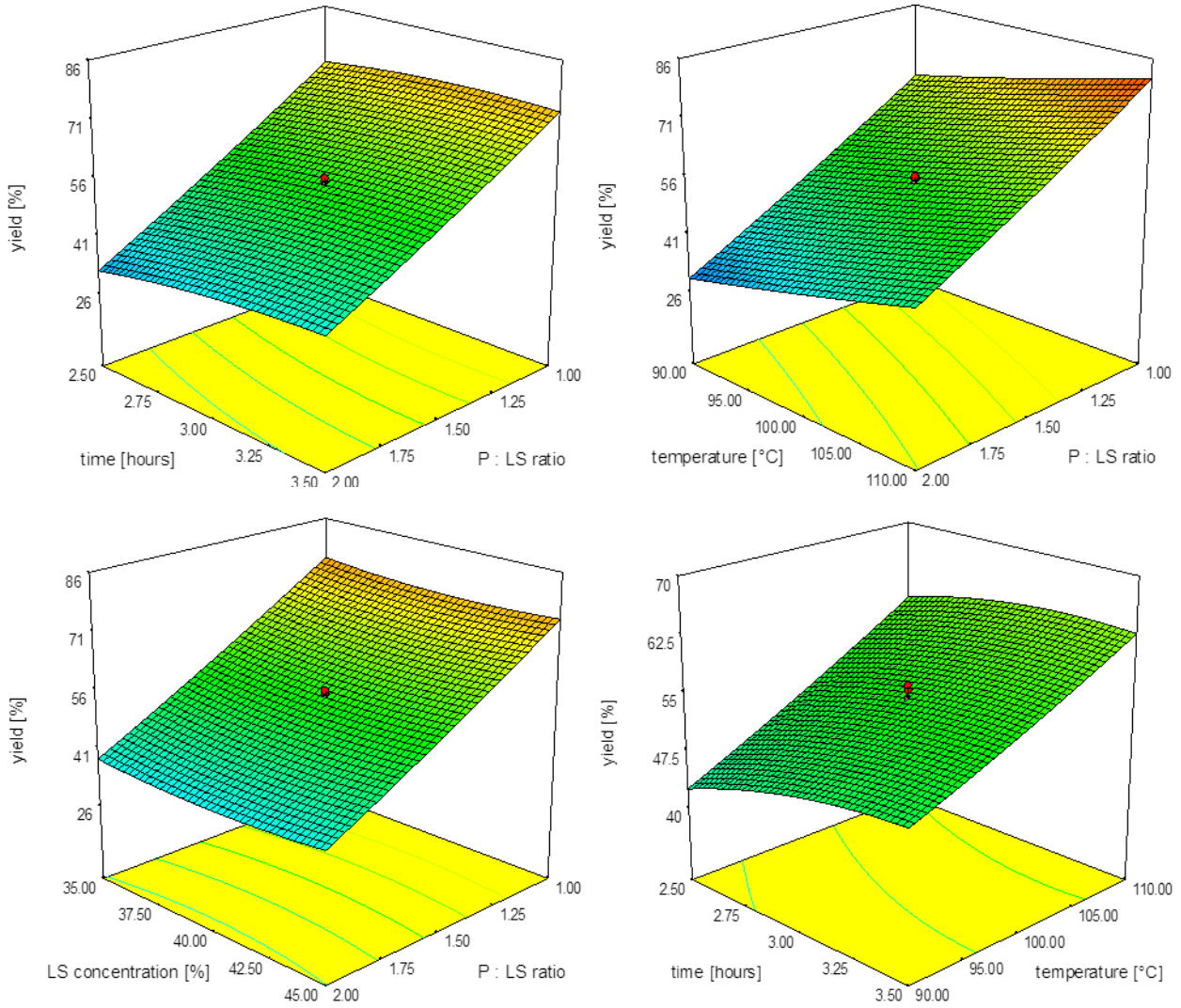
Fig. 3 and Fig. 4 indicate that LS phenolation yields predicted by CCD and BBD mathematical models are greater than 80 % for a P/LS ratio set at 1. In the case of CCD, the reaction yield reached 82 % when the used LS has a concentration of 45 %, and the reaction is conducted at a temperature of 110 °C for 3 hours. For BBD, the reaction yield raised at 86 % when LS concentration was of 35 %, and the reaction took place at 100 °C for 3.5 hours. In other words, the analysis of these data shows that a reaction with a more important concentration of LS requires a higher temperature and a shorter period of time. On the contrary, a greater reaction yield can be reached when a lower concentration of LS is involved and the reaction is conducted at a lower temperature for a longer time. These results are similar with that reported by Alonso et al. (2005) and sustained by the fact that the supplementary experiments carried out in the optimal conditions released by both RSM designs the reaction yields were between 82 % and 85 %. The observed differences between CCD and BBD results can be explained by the ability of BBD to ignore the extreme values chosen for the tested variables presenting, in the same time, the possibility to obtain a reliable mathematical model from fewer experiments.

Table 4. CCD mathematical model accuracy tests results

Source	**-**	***SD***	**-**	***R^2***	***Adj. R^2***	***Pred. R^2***	***PRESS***
Quadratic Model	-	4.18	-	0.9734	0.9486	0.8497	1484.92
Source	***Coefficient Estimate***	**-**	***SS***	***df***	***MS***	***F value***	***p-value Prob > F***
Model	-	-	9614.512	14	686.7508	39.2496	< 0.0001
Intercept	54.49	1.71	-	-	-	-	-
A-P : LS ratio	-18.10	0.85	9614.51	14	686.75	39.25	< 0.0001
B-time	2.48	0.85	7861.55	1	7861.55	449.31	< 0.0001
C-temperature	7.65	0.85	147.36	1	147.36	8.42	0.0109
D-LS concentration	-0.10	0.85	1404.69	1	1404.69	80.28	< 0.0001
AB	1.20	1.05	0.26	1	0.26	0.01	0.9049
AC	0.39	1.05	23.16	1	23.16	1.32	0.2679
AD	0.31	1.05	2.47	1	2.47	0.14	0.7122
BC	-0.89	1.05	1.51	1	1.51	0.09	0.7732
BD	-0.04	1.05	12.80	1	12.80	0.73	0.4059
CD	0.70	1.05	0.02	1	0.02	1.16E-003	0.9733
A^2	0.68	0.80	7.94	1	7.94	0.45	0.5108
B^2	-1.38	0.80	12.80	1	12.80	0.73	0.4059
C^2	0.42	0.80	52.57	1	52.57	3.00	0.1035
D^2	1.54	0.80	4.94	1	4.94	0.28	0.6031
Residual	-	-	64.99	1	64.99	3.71	0.0731
Lack of Fit	-	-	262.46	15	17.50	-	-
Pure Error	-	-	256.25	10	25.62	20.64	0.0019
Cor Total	-	-	6.21	5	1.24	-	-

Table 5. BBD mathematical model accuracy tests results

Source	**-**	***SD***	**-**	***R^2***	***Adj. R^2***	***Pred. R^2***	***PRESS***
Quadratic Model	-	4.231647	-	0.970581	0.941161	0.833244	1421.01
Source	***Coefficient Estimate***	**-**	***SS***	***df***	***MS***	***F value***	***p-value Prob > F***
Model	-	-	8270.775	14	590.7696	32.99129	< 0.0001
Intercept	54.4917	1.7077	-	-	-	-	-
A-P : LS ratio	54.6	1.89	6269.5840	1	6269.5840	350.1223	< 0.0001
B-time	-22.86	1.22	50.7585	1	50.7585	2.8346	0.1144
C-temperature	2.06	1.22	1147.9760	1	1147.9760	64.1083	< 0.0001
D-LS concentration	9.78	1.22	74.1027	1	74.1027	4.1382	0.0613
AB	-2.48	1.22	43.2306	1	43.2306	2.4142	0.1425
AC	-3.29	2.12	74.8225	1	74.8225	4.1784	0.0602
AD	-4.32	2.12	52.1284	1	52.1284	2.9111	0.11
BC	-3.61	2.12	91.2980	1	91.2980	5.0985	0.0404
BD	-4.78	2.12	0.0001	1	0.0001	0.0000	0.9981
CD	-5.00E-03	2.12	98.4064	1	98.4064	5.4955	0.0343
A^2	4.96	2.12	102.7787	1	102.7787	5.7396	0.0311
B^2	3.98	1.66	0.6107	1	0.6107	0.0341	0.8561
C^2	0.31	1.66	195.6399	1	195.6399	10.9254	0.0052
D^2	-5.49	1.66	2.2439	1	2.2439	0.1253	0.7286
Residual	-	-	250.6957	14	17.9068	-	-
Lack of Fit	-	-	245.2168	10	24.5217	17.9027	0.0068
Pure Error	-	-	5.4789	4	1.3697	-	-
Cor Total	-	-	8521.4700	28	-	-	-



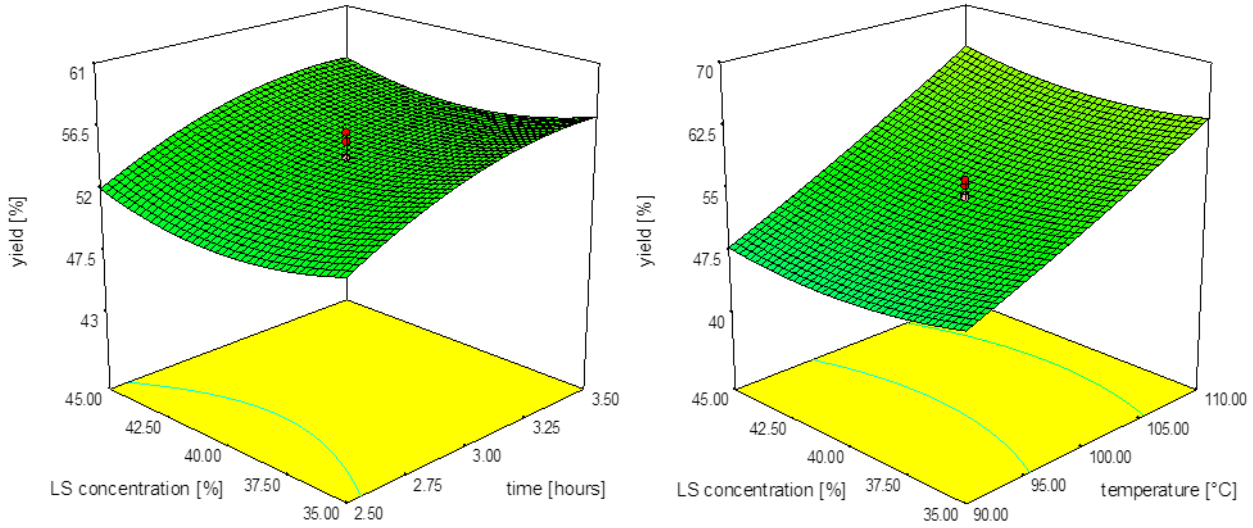
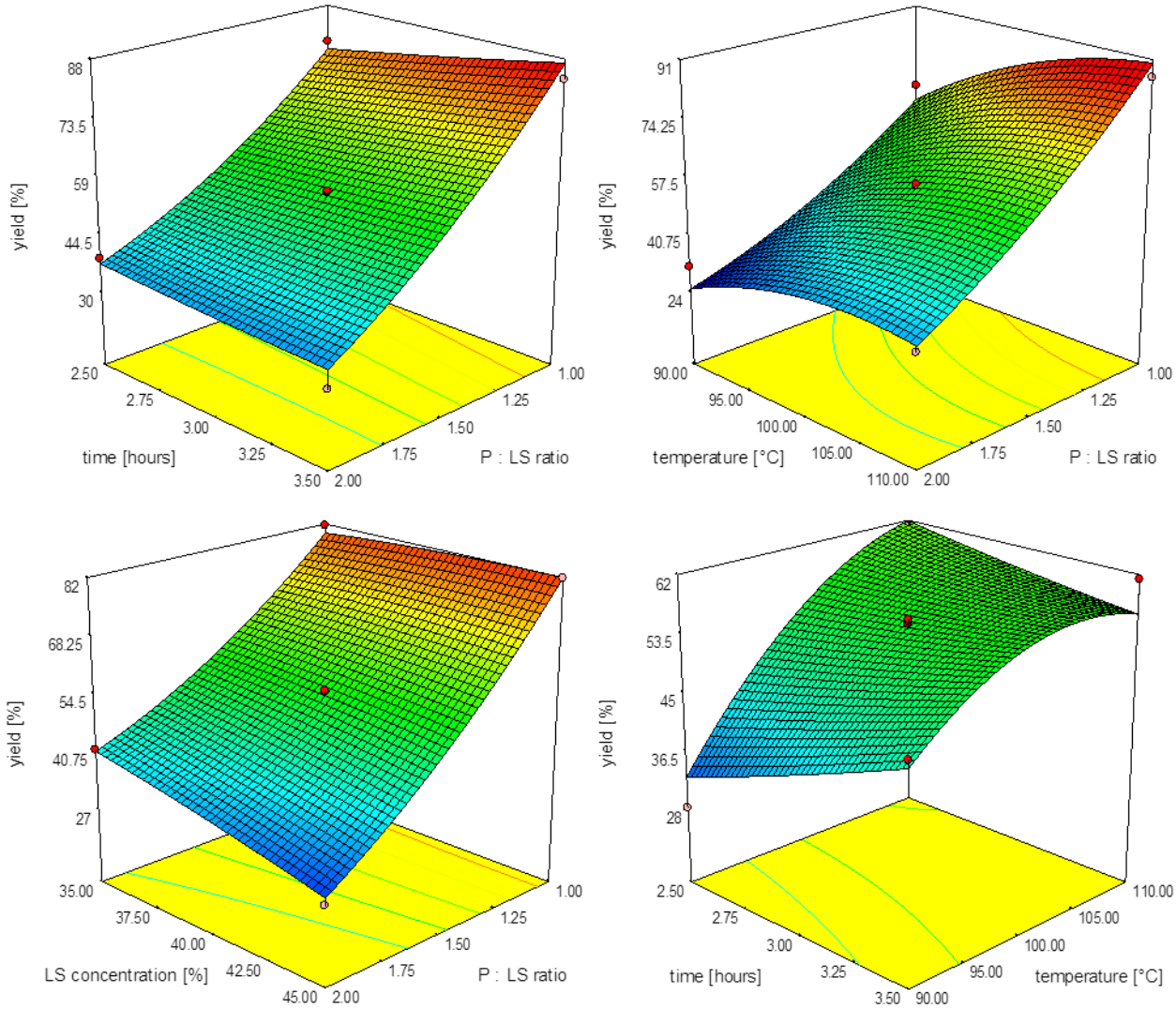


Fig. 1. 3D response surfaces for CCD phenolation reaction yield



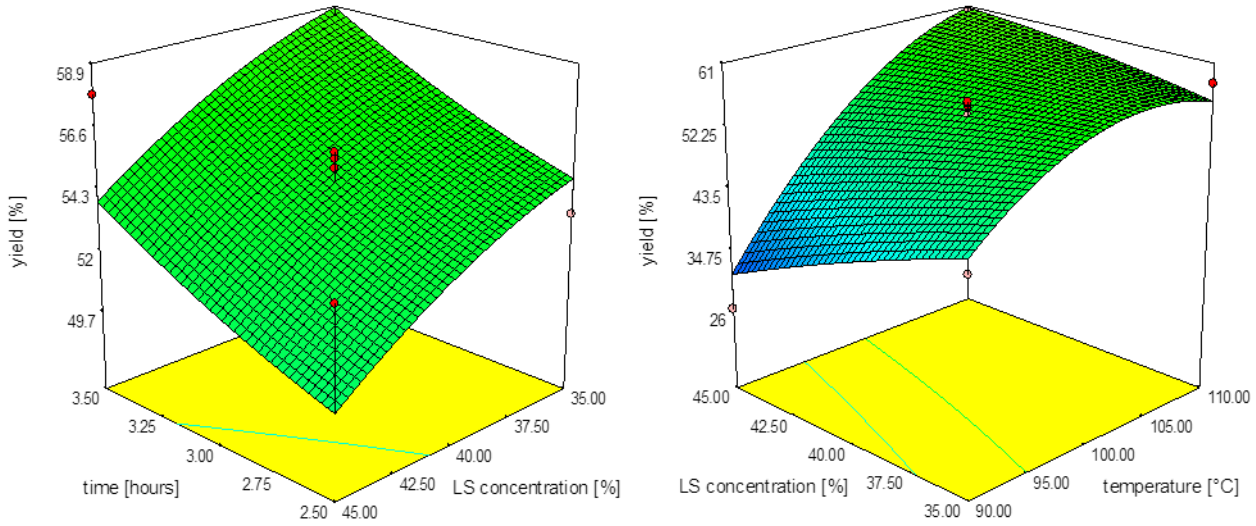


Fig. 2. 3D response surfaces for BBD phenolation reaction yield

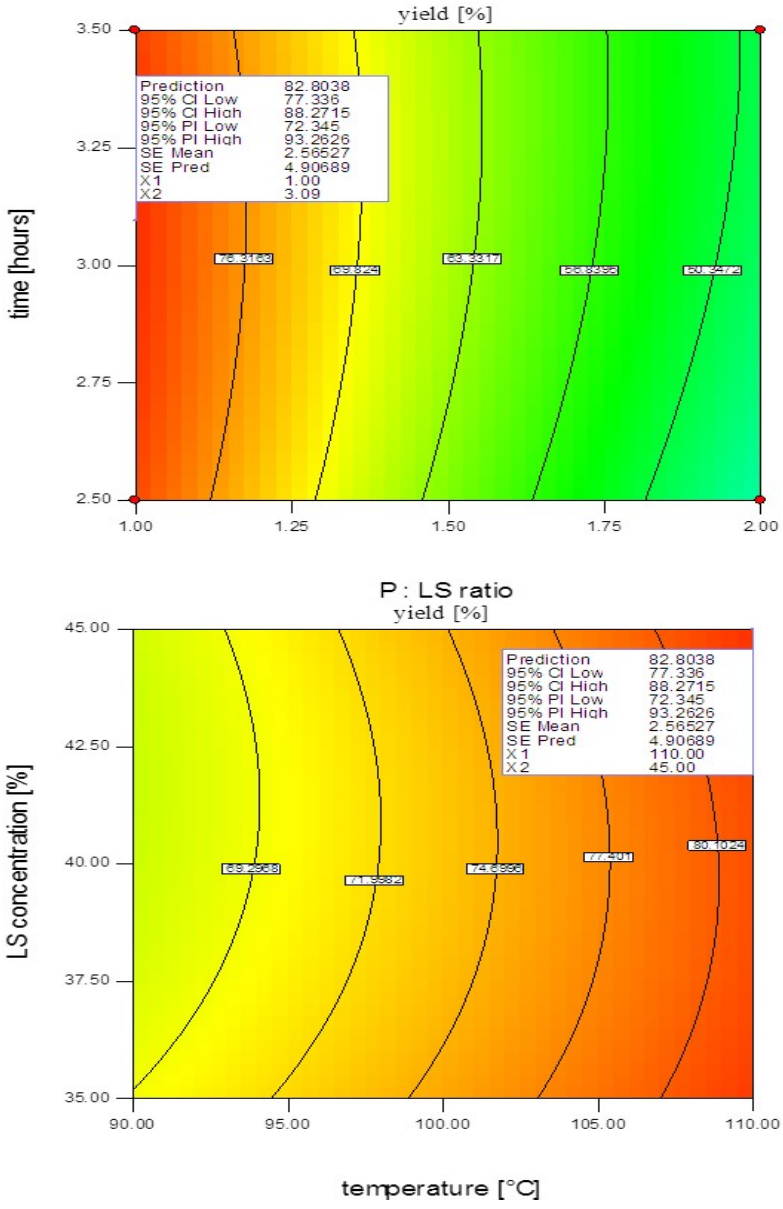


Fig. 3. LS phenolation yield predicted by CCD mathematical model

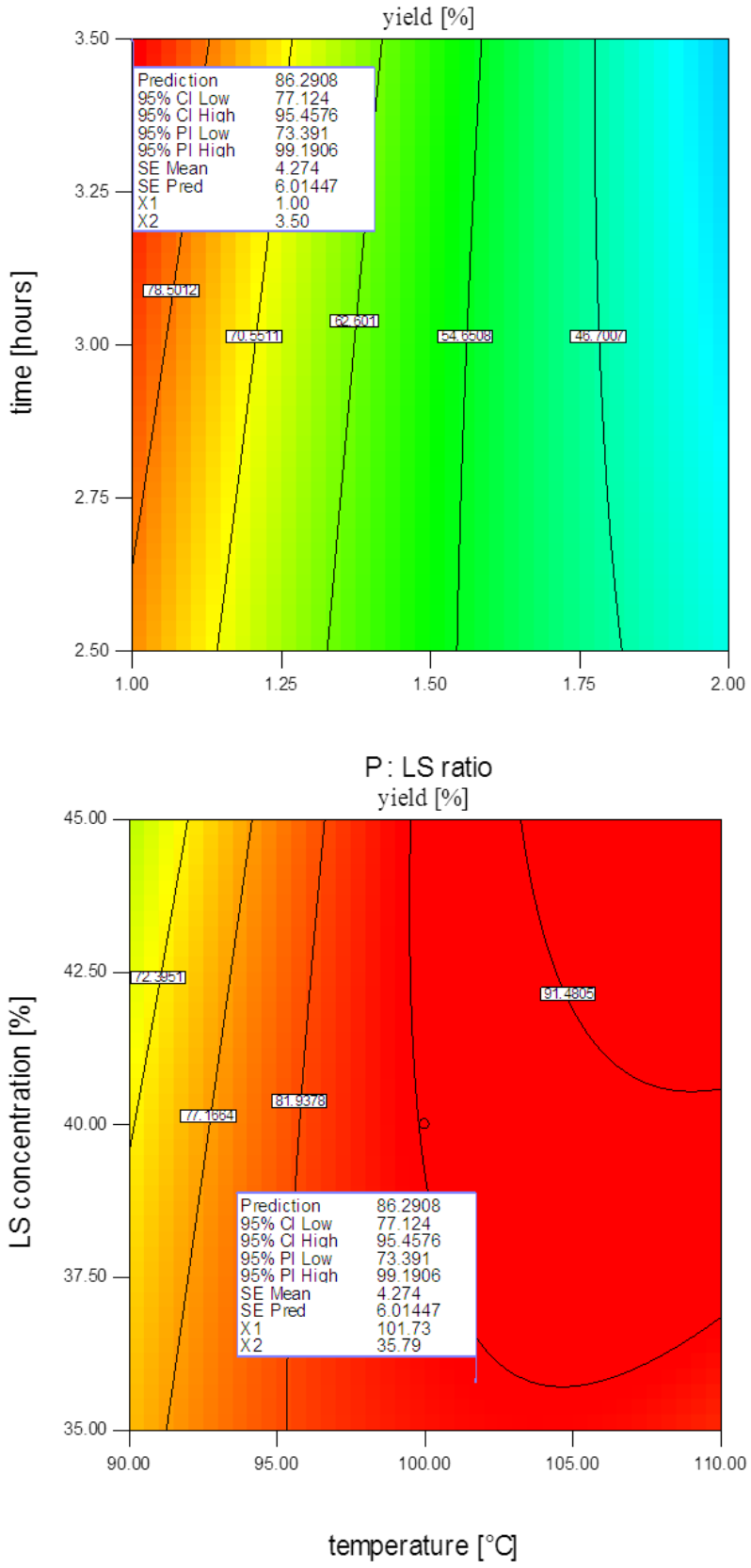


Fig. 4. LS phenolation yield predicted by BBD mathematical model

3.2. ANN modelling

A feed forward multilayer perceptron's ANN based on data included in Table 2 and in Table 3 was established using as input the values of the four parameters influencing the LS phenolation reaction (P/LS ratio, time, temperature and LS concentration) and as output the reaction yields registered in triplicate

for CCD and BBD. This network was chosen due to the fact that it is easy to use, and it is recognized as being able to approximate any input/output map. 70 % of the input data were utilized for network training while the remaining 30 % were equally divided between the cross validation and testing steps. Tests conducted with different number of hidden neurons revealed that when a large number of neurons are considered, the ANN requires a more important period of time to train itself while too few neurons are not sufficient for an appropriate training process. The best results were attained with a hidden layer of 3 neurons: the first one with ten, the second one with five and the third one with four process elements. The developed ANN is given in Fig. 5.

As it can be remarked from Fig. 6, the mean squared error follows a similar path both for training stage and for cross validation at 3000 epochs reaching minimum final values of 0.0283 and of 0.0388 respectively.

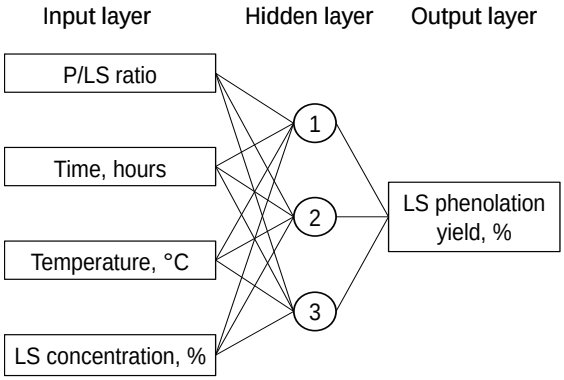


Fig. 5. Schematic representation of the (4 – 3 – 1) neural network (with four neurons in the input layer, three in the hidden layer, and one in the output layer)

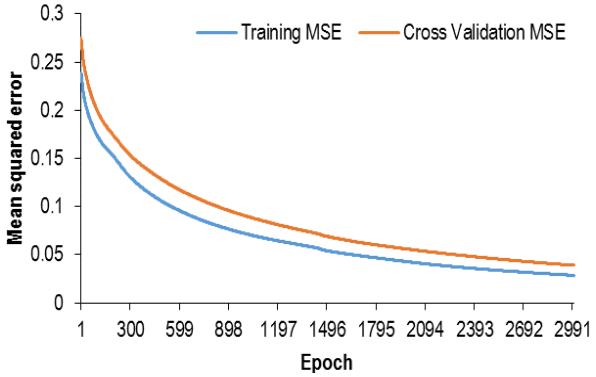


Fig. 6. Comparison between mean squared error (MSE) obtained in training and in cross validation ANN processes

The analysis of experimental recorded LS phenolation yields and of those predicted by ANN (Fig. 7) reveals no significant differences. The selected ANN helps to conclude that the use of all RSM data can provide an accurate model characterized by a MSE of only 5.573, a minimum and a maximum absolute error of 0.0222 and of 7.9258 and by a very high correlation coefficient with a value of 0.9912 suggesting a very good fit with the experimental data.

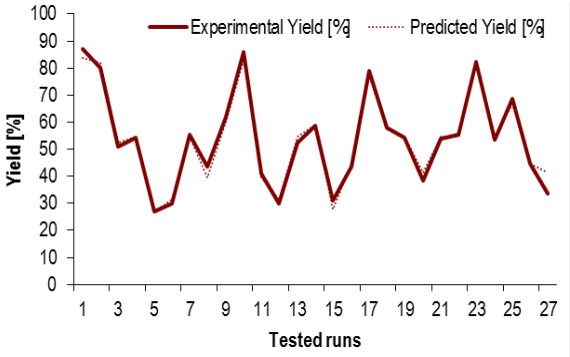


Fig. 7. Evolution of experimental and ANN predicted yield LS phenolation

4. Conclusions

This study was dedicated to the optimization process of the main parameters (phenol – lignosulfonate ratio, time, temperature, lignosulfonate concentration) recognized as affecting the phenolation reaction yield conducted between lignosulfonate waste liquor and phenol.

Two powerful techniques (Response Surface Methodology with Central Composite Design and Box-Behnken Design and Artificial Neural Network) were employed in order to establish the experimental program and to analyze the obtained data. Yields higher than 80 % were recorded when the phenolation was conducted with equal amounts of phenol and lignosulfonate, the lignosulfonate had a concentration varying from 35 % to 45 % and a temperature between 100 °C and 110 °C was insured for more than 3 hours.

Mathematical models generated by RSM (CCD and BBD) were able to accurately estimate the phenol conversion and adduct formation and their adequacy was confirmed by the high similarity existing between the experimental and model predicted data revealed by ANN.

References

Almeida Bezerra M., Santelli R.E., Padua Oliveira E., Silveira Villar L., Escaleira L.A., (2008), Response surface methodology (RSM) as a tool for optimization in analytical chemistry, *Talanta*, **76**, 965-977.

Alonso M.V., Rodriguez J.J., Oliet M., Rodriguez F., Garcia J., Gilarranz M.A., (2001), Characterization and structural modification of ammonic lignosulfonate by methyolation, *Journal of Applied Polymer Science*, **82**, 2661-2668.

Alonso M.V., Oliet M., Rodriguez F., Garcia J., Gilarranz M.A., Rodriguez J.J., (2005), Modification of ammonium lignosulfonate by phenolation for use in phenolic resins, *Bioresource Technology*, **96**, 1013-1018.

Biedermann M., Grob K., (2006a), Phenolic resins for can coatings: I. Phenol-based resol analysed by GC-MS, GC x GC, NPLC-GC and SEC, *LWT – Food Science and Technology*, **39**, 633-646.

Biedermann M., Grob K., (2006b), Phenolic resins for can coatings: II. Resoles based on cresol/phenol mixtures or tert. butyl phenol, *LWT – Food Science and Technology*, **39**, 647-659.

Bu Z., Hu J., Li, B., (2014), Novel silicon-modified phenolic novolac resins: Non-isothermal curing kinetics, and mechanical and thermal properties of their biofiber-reinforced composites, *Thermochimica Acta*, **575**, 244-253.

Cemek B., Rahman S., Rahman A., (2013), Artificial Neural Network for predicting nutrients concentration in runoff from beef cattle feedlot, *Environmental Engineering and Management Journal*, **12**, 2385-2396.

Cheng B., Titterington D.M., (1994), Neural networks: A review from a statistical perspective, *Statistical Science*, **9**, 2-54.

Dharwal R., Kaur L., (2016), Application of artificial neural network: A review, *Indian Journal of Science and Technology*, **9**, 1-8.

Foyer G., Chafi B.-H., Boutevin B., Caillol S., David G., (2016), New method for the synthesis of formaldehyde-free phenolic resins from lignin-based aldehyde precursors, *European Polymer Journal*, **74**, 296-309.

Greco A., Ferrari F., Maffezzoli A., Delogu P., Velardi R., Timo A., Tarzia A., Marseglia A., Calo M., (2016), Solubility and durability of cardanol derived plasticizers for soft PVC, *Environmental Engineering and Management Journal*, **15**, 1989-1995.

Hirano K., Asami M., (2013), Phenolic resins – 100 years of progress and their future, *Reactive & Functional Polymers*, **73**, 256-269.

Hu L., Pan H., Zhou Y., Zhang M., (2011), Methods to improve lignin's reactivity as a phenol substitute and as replacement for other phenolic compounds: A brief review, *BioResources*, **6**, 3515-3525.

Hu L., Zhou Y., Zhang M., Liu R., (2012), Characterization and properties of a lignosulfonate-based phenolic foam, *BioResources*, **7**, 554-564.

Koricic K., Kusic H., Koprivanac N., Papic S., (2016), Mineralization of salicylic acid in water by catalytic ozonation, *Environmental Engineering and Management Journal*, **15**, 151-166.

Li W., Jing S., Wang S., Wang C., Xie X., (2016), Experimental investigation of expanded graphite/phenolic resin composite bipolar plate, *International Journal of Hydrogen Energy*, **41**, 16240-16246.

Martin C., Ronda J.C., Cadiz V., (2006), Boron-containing novolac resins as flame retardant materials, *Polymer Degradation and Stability*, **91**, 747-754.

Meireles M.R.G., Almeida P.E.M., Godoy Simoes M., (2003), A comprehensive review for industrial applicability of artificial neural networks, *IEEE Transactions on Industrial Electronics*, **50**, 585-601.

Noparvar-Qarebagh A., Roghani-Mamaqani H., Salami-Kalajahi M., (2016), Novolac phenolic resin and graphene aerogel organic-inorganic nanohybrids: High carbon yields by resin modification and its incorporation into aerogel network, *Polymer Degradation and Stability*, **124**, 1-14.

Perez J.M., Rodriguez F., Alonso M.V., Oliet M., Echeverria J.M., (2007), Characterization of a novolac resin substituting phenol by ammonium lignosulfonate as filler or extender, *BioResources*, **2**, 270-283.

Rajakovic-Ognjanovic V.N., Jovanovic B.M., Zijovinovic D.Z., Rajakovic L.V., (2014), Challenging analytical task: Analysis and monitoring of arsenic species in water, *Environmental Engineering and Management Journal*, **13**, 2275-2282.

Roslan R., Zakaria S., Chia C.H., Boehm R., Laborie M.-P., (2014), Physico-mechanical properties of resol phenolic adhesives derived from liquefaction of oil palm empty fruit bunch fibres, *Industrial Crops and Products*, **62**, 119-124.

Shirneshan A., Almassi M., Ghobadian B., Borghei A.M., Najafi G., (2016), Response Surface Methodology (RSM) based optimization of biodiesel-diesel blends and investigation of their effects on diesel engine operating conditions and emission characteristics, *Environmental Engineering and Management Journal*, **15**, 2771-2780.

Shudo Y., Izumi A., Hagita K., Nakao T., Shibayama M., (2016), Large-scale molecular dynamics simulation of crosslinked phenolic resins using pseudo-reaction model, *Polymer*, **103**, 261-276.

Shudo Y., Izumi A., Hagita K., Nakao T., Shibayama M., (2017), Structure-mechanical property relationships in crosslinked phenolic resin investigated by molecular dynamics simulation, *Polymer*, **116**, 506-517.

Wang J., Deng X., Zhang H., Zhang D., Duan H., Lu L., Song J., Tian L., Song S., Zhang S., (2017), Synthesis of carbon nanotubes via Fe-catalyzed pyrolysis of phenolic resin, *Physica E*, **86**, 24-35.

Wu H., Yin R., Qian L., Zhang Z., (2017), Three-dimensional graphene network/phenolic resin composites towards tunable and weakly negative permittivity, *Materials and Design*, **117**, 18-23.

Xiang Y., Wang L., Xiang Y., (2015), Optimization of ultrasonic extraction conditions for excess sludge protein using Response Surface Methodology, *Environmental Engineering and Management Journal*, **14**, 1151-1159.

Yang X., Frazier C.E., (2016), Influence of organic fillers on rheological behavior in phenol-formaldehyde adhesives, *International Journal of Adhesion & Adhesives*, **66**, 93-98.

Zhao X., Lai S., Liu H., Gao L., (2009), Preparation and characterization of activated carbon foam from phenolic resin, *Journal of Environmental Sciences Supplement*, S121-S123.

Zulfikar M.A., Mariske E.D., Djajanti S.D., (2012), Adsorption of lignosulfonate compounds using powdered eggshell, *Songklanakarin Journal of Science and Technology*, **34**, 309-316.