Scientific paper

THE QUALITY ANALYSES OF OLIVE CAKE FUEL PELLETS - MATHEMATICAL APPROACH

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SUMMARY

This article investigates the effect of processing parameters (conditioning temperature and binder content), on final quality of produced agro-pellets for heat energy generation, obtained from four different olive cultivars using different technological parameters. Technological, physical and chemical properties of pellets (carbon, hydrogen, nitrogen and sulphur content, particle density, abrasion length, moisture, ash content, higher and lower heating values, fixed carbon and volatile matter content) have been determined to assess their quality. The performance of Artificial Neural Network (ANN) was compared with the performance of second order polynomial (SOP) model, as well as with the obtained experimental data in order to develop rapid and accurate mathematical model for prediction of final quality parameters of agro-pellets. SOP model showed high coefficients of determination (r^2), between 0.692 and 0.955, while ANN model showed high prediction accuracy with r^2 between 0.544 and 0.994.

KEY WORDS: olive cake; olive cultivar; agro-pellets; pelleting; mathematical model

INTRODUCTION

Due to global reduction in fossil energy sources, investigations have turned to renewable sources. Among renewable energy sources, biomass particularly stands out because it can be used to cover a variety of energy needs and it can also be stored, unlike other renewable energy sources, [1]. The use of biomass as an energy source also enables closing of the carbon cycle, which is not the case when fossil fuels are used, [2].

Widely available biomass is agricultural waste. In order to meet the world's trends in waste utilization and valorisation, olive oil mill waste, i.e. olive cake, has been used in this research as an potential energy source (prepared as agro-pellets). Due to the initiatives and stimulants from the Croatian government olive oil production has been increasing in the last ten years. Therefore, the quantities of olive cake have also risen. Croatia currently produces about 38,000 tons of olives per year, with the average yield of 2.2 t/ha which results with approximately 16,000 tons of fresh olive cake, [3]. That is a large quantity considering the narrow coastal area of Croatia where olives are grown. This kind of waste has a negative influence on the environment due to its chemical composition and therefore cannot be disposed to the conventional landfill. One of the solutions for olive cake disposal is production of fuel pellets. Pelletized material is much easier to manipulate and store, moreover it has higher density and better heating value/volume ratio, [4].

Results of quality analyses of olive cake pellets obtained in a previous investigation were used in this paper, [5]. Improved mathematical approach of the previously obtained results was applied in order to more accurately analyse the quality of the produced agro fuel pellets in order to optimize the pelleting process. The goal is to obtain high quality fuel pellets which are in accordance with European standards for fuel pellets and are produced with no unnecessary costs.

Response surface methodology (RSM) is used as an effective tool for optimizing a variety of processes, [6-8].The main advantage of RSM is reduced number of experimental runs that provide sufficient information for statistically valid results. The RSM equations describe effects of the test variables on the observed responses, determine test variables interrelationships and represent the combined effect of all test variables in the observed responses, enabling the experimenter to make efficient exploration of the process.

Nonlinear models are found to be more suitable for real process simulation. Response Surface Methodology (RSM) and Artificial Neural Network (ANN) models have gained momentum for modelling and control of processes, [9, 10].

ANN models are recognized as a good modelling tool since they provide the empirical solution to the problems from a set of experimental data, and are capable of handling complex systems with nonlinearities and interactions between decision variables, [11]. The specific objective of this study was to investigate the effect of olive cultivar, conditioning temperature and binder content on technological, physical and chemical properties of pellets (carbon, hydrogen, nitrogen and sulphur content, particle density, abrasion length, moisture, ash content, higher and lower heating values, fixed carbon and volatile matter content). The performance of ANN was compared with SOPs, as well as to experimental data in order to develop rapid and accurate prediction models.

The current study intends to investigate the effects of conditioning temperature and added binder content on the final quality of agro-pellets produced from four different olive cultivars using different technological treatments. Also, this investigation is focused on finding the appropriate mathematical models for carbon, hydrogen, nitrogen and sulphur content, particle density, abrasion and length, and also moisture and ash content, higher and lower heating value (HHV and LHV), fixed carbon and volatile matter content, regarding observed process parameters: conditioning treatment and added binder content.

MATERIALS AND METHODS

Raw-material

Pellets from four different olive cake cultivars were used in this research; 'Istarska Bjelica', 'Buža', 'Leccino' i 'Pendolino'. Olive cake was obtained from an olive oil mill in Istria, Croatia. Parameters which were varied during preparation of olive cake for pelleting were steam conditioning treatment (unconditioned, conditioned at 50 °C, and conditioned at 80 °C) and amount of added binder (no binder, 1 % of added binder, and 2 % of added binder). The treatments resulted in nine combinations for each of four cultivars used, making a total of 36 combinations for pelleting, which are presented in Table 1. Detailed description of the preparation of the material and the process of pelleting of the olive cake is given in a previous paper, [5].

Table 1.

Analyses of the pellets

Proximate analyse that were done on the samples were: moisture content, [12], ash content, [13], fixed carbon (calculated by difference between 100 and the sum of volatile matter, ash and moisture) and volatile mater, [14]. Samples were analysed for ultimate composition: content of C, H, N, [15] and S, [16], HHV and LHV, [17].

Physical characteristics determined in this study were abrasion, density and length of pellets. Abrasion was determined with abrasion test device “Pfost” (Bühler, Switzerland). Density was analysed using the hydrostatic method on the analytical balance, with ethanol as a medium for wetting. Length of the pellets was measured by calliper. Detailed description of the preformed measurements is given in our previous work, [5].

Mathematical modelling

Descriptive statistical analyses for all the obtained results have been expressed as the mean ± standard deviation (SD). Furthermore, the evaluation of one-way ANOVA and PCA analyses of the obtained results has been performed using StatSoft Statistica 10.0® software. Collected data have been subjected to one-way analysis of variance (ANOVA) for the comparison of means, and significant differences are calculated according to post-hoc Tukey's HSD ("honestly significant differences") test at $p<0.05$ significant level, 95% confidence limit. All data are reported as means ± standard deviations.

Response Surface Methodology

The experimental data used for the study of experimental results were obtained using a 4×3^2 full factorial experimental design (3 levels-2 parameter), with 9 runs (4 blocks, for each of four different cultivars), according to Response surface methodology, [18]. It was used to design the final product quality, considering two factors: conditioning temperature and added binder content.

The following second order polynomial (SOP) model was fitted to the experimental data. Thirteen models of the following form were developed to relate thirteen responses (Y) and two process variables (X), for each of four different olive cultivars:

$$Y_k^l = \beta_{k0}^l + \sum_{i=1}^{2} \beta_{ki}^l \cdot X_i + \sum_{i=1}^{2} \beta_{kii}^l \cdot X_i^2 + \beta_{k12}^l \cdot X_1 \cdot X_2, \text{ k=1-13, l=1-4,} \quad (1)$$

where: β_{k0}^l, β_{ki}^l, β_{kii}^l, β_{k12}^l are constant regression coefficients; Y_k^l, either C, H, N or S content, particle density, abrasion and length, moisture and ash content, HHV, LHV, fixed carbon or volatile matter content; X_1 - conditioning temperature; X_2 - binder content.

Artificial Neural Network

The database for ANN was randomly divided to: training data (60%), cross-validation (20%) and testing data (20%). The cross-validation data set was used to test the performance of the network, while training was in progress as an indicator of the level of generalization and the time at which the network has begun to over-train. Testing data set was used to examine the network generalization capability. To improve the behaviour of the ANN, both input and output data were normalized. In order to obtain good network behaviour, it is necessary to make a trial and error procedure and also to choose the number of hidden layers, and the number of neurons in hidden layer(s). A multi-layer perceptron models (MLP) consisted of three layers (input, hidden and output). Such a model has been proven as a quite capable of approximating nonlinear functions, [19] giving the reason for choosing it in this study. In this work the number of hidden neurons for optimal network was ten. Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm was used for ANN modelling.

After defining the architecture of ANN, the training step was initiated. The training process was repeated several times in order to get the best performance of the ANN, due to a high degree of variability of parameters. It was accepted that the successful training was achieved when learning and cross-validation curves approached zero. Testing was carried out with the best weights stored during the training step. Coefficient of determination (r^2) and sum of squares (SOS) were used as parameters to check the performance (i.e. the accuracy) of the obtained ANNs. After the best behaved ANN was chosen, the model was implemented using an algebraic system of equations to predict carbon, hydrogen, nitrogen and sulphur content, particle density, abrasion and length, and also moisture and ash content, higher and lower heating value (HHV and LHV), fixed carbon and volatile matter content.

Sensitivity analysis

Sensitivity analysis is a sophisticated technique which is necessary to use for studying the effects of observed input variables and also the uncertainties in obtained models and general network behaviour. Neural networks were tested using sensitivity analysis, to determine whether and under what circumstances obtained models might result in an ill-conditioned system, [20]. On the basis of developed ANN models, sensitivity analysis was performed in order to more precisely define the influence of processing variables on the observed outputs. The infinitesimal amount (+0.0001%) has been added to each input variable, in 10 equally spaced individual points encompassed by the minimum and maximum of the train data. These signals were normally distributed with a constant intensity and frequency. It was used to test the model sensitivity and measurement errors.

Normal standard score

Normal scores have been calculated for each assay, and were used for complex comparison of observed samples, regarding their technological, physical and chemical properties listed in Table 3 and Table 4. The ranking procedure between different samples has been performed based upon the ratio of raw data and extreme values for each applied assay [5, 21, 22], according to these equations:

$$\bar{x}_i = 1 - \frac{\max_i x_i - x_i}{\max_i x_i - \min_i x_i}, \quad \forall i \text{ in case of "the higher, the better" criteria, or}$$

$$\bar{x}_i = \frac{\max_i x_i - x_i}{\max_i x_i - \min_i x_i}, \quad \forall i \text{, in case of "the lower, the better" criteria.}$$

where x_i represents the raw data.

Unlike others variables, normalized scores for moisture and length have been evaluated according to optimal values, using trapezoidal function, as follows:

$$A(x,a,m,n,b) = \begin{cases} a \le x < m, & \dfrac{x-a}{m-a} \\ m \le x < n, & 1 \\ n \le x < b, & 1 - \dfrac{x-n}{b-n} \end{cases}, \quad (2)$$

where x is whether moisture and length parameter, and the values of *a*, *b*, *m* and *n* are function parameters. Interval *a* - *b* represent the range in which measured values occur in the experiment (minimum and maximum values), while range *m* - *n* is the proposed optimal values range for response variables, chosen for technological reasons. An optimization with procedure was performed using MicroSoft Excel 2007 to determine the workable optimum conditions for agro-pellets production.

RESULTS AND DISCUSSION

The agro-pellets production was studied in terms of common technological, physical and chemical parameters, i.e. C, H, N and S content, particle density, abrasion and length, moisture and ash content, HHV, LHV, fixed carbon and volatile matter content.

Each of the process variables has been coded, as shown in Table 2, and these codes are used for easier representation of experimental data.

Table 2.

Response Surface Methodology

Ultimate analysis

Chemical characteristics (C, H, N and S content) of four different cultivars (Bjelica, ‘Buža’, ‘Leccino’ and ‘Pendolino’) of olive cake are presented in Table 3. Tukey's HSD test showed significant differences for most cases.

The analysis of variance (ANOVA), exhibits the significant independent variables as well as interactions of these variables. In this article, ANOVA was conducted by StatSoft Statistica, ver. 10 to show the significant effects of independent variables to the responses, and to show which of responses were significantly affected by the varying treatment combinations (Table 5).

The analysis revealed that the linear terms contributed substantially in all cases to generate a significant SOP model. The SOP models for all variables were found to be statistically significant and the response surfaces were fitted to these models.

The most influential variable for SOP model calculation was found to be the type of olive cultivar. Non-linear terms of SOP models have been found most influential for C and H content, while linear terms have been most important for N and S content calculation. The influences of temperature and binder content are also observed, but far less important than the cultivar type.

Nitrogen content is mostly affected by cultivar type, but the effects of conditioning temperature and binder content have also been observed. Sulphur content is mostly affected by cultivar type, but the influence of linear and quadratic terms of conditioning temperature and binder content have been also noticed on $p<0.05$ statistically significant level.

Nitrogen and sulphur content should be especially monitored while these elements can be the most harmful for the environment due to emission of polluting gasses during combustion. Therefore it is desirable that their content is as low as possible. N content was in range from 0.69 to 1.07 (Table 3), which is slightly lower than in literature data, [23], and the minimum content has been observed in pellets produced from 'Istarska Bjelica' cultivar. According to European standards for fuel pellet quality the highest allowed concentration of nitrogen is 1.0 %, [24], therefore it is evident that these pellets are mostly in acceptable range. It is known that wood as a raw material for the production of pellets has a lower proportion of nitrogen than agricultural biomass, [25]. Johansson et al., [26], found only 0.08 % of nitrogen in wood pellets. Coal on the other hand has about 1% nitrogen, [27], which is very similar to the values obtained for olive cake pellets. Therefore olive cake pellets will cause equal nitrogen oxides emissions as coal.

Produced pellets contained approximately 0.07 – 0.08 % of sulphur (Table 3), which is consistent with data in the literature, [23], and highest allowed content by EU standards is 0.04, [24]. Minimum sulphur content has been observed in pellets made of 'Istarska Bjelica' cultivar. Produced pellets exceed the proscribed boundaries, but according to [28], there are pellets that are allowed 0.08 % S. Very small amounts of S can be found in wood and wood pellets [26, 29], while on the other hand coal has much higher contents of S: 2 – 3 %, [27, 30]. Therefore biomass produces significantly less sulphur oxides during combustion.

Carbon content is affected by both quadratic and linear term in SOP model (statistically significant at $p<0.05$ level), while the influence of binder content has been found to be insignificant. Besides cultivar type, the most influential terms in SOP model of hydrogen content are linear terms of conditioning temperature and binder content ($p<0.05$), and also the nonlinear terms. As presented in Table 3, carbon content varied in the range from 53.53 to 57.68 % which is consistent with the literature, while hydrogen was also in common values: 7.26 – 8.22 [23, 3]. Slightly lower contents of carbon and hydrogen have been noticed in pellets made of 'Istarska Bjelica' cultivar, compared to other cultivars. Carbon and hydrogen are not limiting factors, thus their amount is not proscribed by standards. Moreover it is desirable that material has higher content of C and H, while it contributes to higher heating energy.

Physical properties

Physical properties (particle density, abrasion and length) are also presented in Table 3, and the ANOVA calculation in Table 5. Statistically significant differences have been found in most cases, mostly influenced by process temperature ($p<0.05$). Binder content has been found as most influential variable for particle density calculation, while both linear and quadratic terms of conditioning temperature have been found statistically significant at $p<0.05$ level. Cultivar type showed minor impact on particle density, but still statistically significant. Particle density of all samples was above 1.12 g/cm^3 which is the value proscribed by several EU standards, [28]. The density of the pellets treated with the same conditioning treatment increased with the addition of binder, as shown in Table 3. Both abrasion and length calculation are most influenced by conditioning temperature, while cultivar type terms have been found statistically significant.

Abrasion of the pellets varied from 3.43 to 15.92 %. The highest allowed level of abrasion in fuel pellets is 10.0 % according to [28]; therefore most of the produced pellets fall into this range. Conditioning treatment and addition of binder decreases abrasion of all samples, because conditioning increases moisture content of the material as well as exposes it to elevated temperatures which facilitate particle binding, [32, 33].

Table 3.

Proximate analysis

The results of proximate analysis (moisture and ash content, HHV, LHV, fixed carbon and volatile matter content) of oil cake is presented in Table 4, and the ANOVA calculation of these parameters is presented in Table 5. Statistically significant differences of samples have been found in most cases, according to Tukey's HSD test, for various observed assays. Conditioning treatment has been the most important variable for moisture content and fixed carbon.

Ash content and HHV were mostly impacted by cultivar type, while LHV was mostly influenced by conditioning and binder content. ANOVA calculation showed complex influence of linear and nonlinear terms for variables: fixed carbon and volatile matter. Recommended moisture content is up to 10 %, which was the case for all pellets except the ones made from material conditioned at 80 °C. Ash content varied in range: 1.54 – 1.95 %, which is in boundaries proscribed by EU standards, [28], where the highest allowed value is 6.0 % of ash. Lower ash content increases heating value and improves combustion properties. LHV proscribed by EU standards advise values in range: from > 16.0 to > 18 MJ/kg. All of the samples had LHV higher than 20 MJ/kg and thus meet the proscribed norms.

Table 4.

Also shown in Table 5 is the residual variance where the lack of fit variation represents other contributions except for the higher order terms. A significant lack of fit generally shows that the model failed to represent the data in the experimental domain at which points were not included in the regression, [34]. All SOP models had insignificant lack of fit tests, which means that all the models represented the data satisfactorily.

The coefficient of determination, r^2, is defined as the ratio of the explained variation to the total variation and is explained by its magnitude, [18]. It is also the proportion of the variability in the response variable, which is accounted for by the regression analysis. A high

r^2 is indicative that the variation was accounted and that the data fitted satisfactorily to the proposed model (SOP in this case).

The r^2 values for C (0.753), H (0.765), N (0.892) and S content (0.845), particle density (0.841), abrasion (0.930) and length (0.899), moisture and ash content (0.955 and 0.719), HHV, LHV, fixed carbon and volatile matter content (0.736, 0.697, 0.774 and 0.692, respectively) were satisfactory and show the good fitting of the model to experimental results. Table 6 shows the regression coefficients for the response SOP models of C, H, N and S content, particle density, abrasion and length, moisture and ash content, HHV, LHV, fixed carbon and volatile matter content used by Eq. (1) for predicting the values.

Table 5.

Artificial Neural Network

All variables considered in the RSM, were also used for the ANN modelling. Determination of the appropriate number of hidden layers and number of hidden neurons in each layer is one of the most critical tasks in ANN design. The number of neurons in a hidden layer depends on the complexity of the relationship between inputs and outputs. As this relationship becomes more complex, more neurons should be added, [35].

The optimum number of hidden neurons was chosen upon minimizing the difference between predicted ANN values and desired outputs, using SOS during testing as performance indicator. Used multi-layer perceptron models (MLPs) were marked according to StatSoft Statistica's notation. MLP was followed by number of inputs, number of neurons in the hidden layer, and the number of outputs. According to ANNs summary, it was noticed that the optimal number of neurons in the hidden layer for responses prediction was 9 (network MLP 3-9-13), when obtaining high values of r^2 (0.914, 0.890 and 0.825 for training, testing and validation period, respectively) and low values of SOS (0.059, 0.084 and 0.108 for training, testing and validation period, respectively). The used activation functions were: hyperbolic tangent for hidden layer and logistic, for output layer; used training algorithm was BFGS 149. Performances of the optimal ANN, regarding r^2 between experimental measurements and predicted results is presented on Table 6.

Table 6.

Optimal network, used for prediction of response variables was able to predict reasonably well the output for a broad range of the process variables. The predicted values were very close to the experimental (target) values in most cases, in terms of r^2 value for both SOP and ANN models.

It can be seen that the r^2 value for ANN model is greater than this associated with the SOP model (except those for HHV and LHV calculation). Generally, ANN model is more complex (186 weights-biases for calculation) than SOP, and it has performed better fitting of experimental data due to the high nonlinearity of the developed system, [36, 37].

The mean and the standard deviation of residuals have also been analysed. The mean and standard deviation (SD) of residuals is presented in Table 7. These results showed a good approximation to a normal distribution around zero with a probability of 95% (2 × SD), which means a good generalization ability of ANN model for the range of observed experimental values.

Table 7.

Figure 1.

Sensitivity analysis

In order to or assess the effect of changes in the outputs due to the changes in the inputs, a sensitivity analysis was performed. The greater effect observed in the output imply that greater sensitivity is presented with respect to the input, [38]. Sensitivity analysis has been performed to test an infinitesimal change in an input value in 10 equally spaced individual points, ranged by the minimum and maximum of the observed assay, in order to explore the changes in observed outputs. It is also used to test the model sensitivity and measurement errors.

Figure 2.

The influence of the input over the output variables, i.e. calculated changes of output variables for infinitesimal changes in input variables, is shown on Figure 3. Obtained values corresponded to level of experimental errors, and also showed the influence of cultivar type, temperature and binder content on response variables.

According to Figure 3, particle density is mostly influenced by cultivar type, showing higher values for ‘Leccino’ and ‘Pendolino’, then for 'Istarska Bjelica' and ‘Buža’. Temperature becomes more influential at the maximum of input space, decreasing the particle density, while binder content slightly increases this parameter at the maximum of input space.
Temperature of the treatment seems to be the most influential variable for abrasion and the length of pellets, especially for temperatures close to minimum of input space (abrasion is decreased, while the length is being increased for small changes in temperature). 'Istarska Bjelica' and ‘Buža’ showed tendency for being more abrasive. The olive cultivar type is the most important for prediction of ash content, as well as C, H, N and S content, as expected. HHV, fixed carbon and volatile matter are also mostly influenced by cultivar type, but the final value of these responses could be increased if conditioned at higher temperatures. All of these findings are in accordance with ANOVA analysis, as well as with experimental measurements.
Normal standard score optimization of the thirteen response variables was accomplished in order to find the processing variables (conditioning temperature and binder content), that give optimal values of response variables. Trapezoidal membership function was used as optimization method, according to Eq. 2, in which *a* - *b* covered the complete interval (minimum and maximums), where obtained values for separately tested samples were found during the experiment, and m - n represented the optimal values for observed product group (written in Tables 3 and 4). The "higher the better" or the "lower the better" criteria have been used according to the sign in "Polarity" raw in Tables 3 and 4, while moisture and length parameters have been represented by their optimal values.
The objective function (*F*) is the mathematical function whose maximum would be determined, by summing the FSE results for of the thirteen models, according to Eq. 1. Each response variable (C, H, N and S content, particle density, abrasion and length, and also moisture and ash content, HHV, LHV, fixed carbon and volatile matter content) has equal weight, when calculating the function *F*.
The maximum of function F represents the optimal parameters for processing parameters, and also the optimum for response variables. The three-dimensional graphs for four different olive cultivars, were obtained using objective function to determine optimum production conditions, regarding production parameters (conditioning temperature and binder content), Fig. 1. If the value of membership trapezoidal function is close to 1, it shows the tendency of tested processing parameters of being optimal. Three-dimensional plots were drawn for calculated

FSE data visualization (white coloured points) and for the purpose of observation. F functions were plotted using RSM procedure, and the obtained coefficients of determinations in ANOVA analysis, regarding the accuracy of fitting, were: 0.883 (for 'Istarska Bjelica'), 0.865 (for 'Buža'), 0.956 (for 'Leccino') and 0.973 (for 'Pendolino').

FSE analysis showed that the best results were obtained with conditioning treatment at 50 °C and without binder addition for cultivar 'Buža' (maximum *F*=0.66), Fig. 1b. 'Istarska.Bjelica', (Fig. 1a) also had satisfactory results, with largest *F*=0.64, for lower temperature regime (closer to 40 ^{o}C), and increased binder content (approx. 2%). Other two cultivars ('Pendolino' (Fig. 1d) and 'Leccino' (Fig. 1c)) had somewhat lower results with maximum *F* value of 0.63, with no conditioning and with binder content of 2%.

Generally the analysed agro-pellets had good quality for energy utilization and almost all characteristics were within the limits of EU standards. Although these standards are primary intended to regulate characteristic of pellets made from wood and wood residues, the produced olive cake pellets were almost as good.

Figure 3.

CONCLUSION

Investigation concerning the utilization of olive cake cultivars 'Istarska Bjelica', 'Buža', 'Leccino' and 'Pendolino' for production of fuel agro-pellets, suggest following conclusions.

The applied Response Surface Methodology of data gave accurate results concerning pellet quality. The obtained models presented good fitting to experimental results and had presented them satisfactory.

Olive cultivar was the variable which had had significant influence on all the measured parameters, especially on the ultimate analyses results. Physical characteristic were also significantly affected by conditioning temperature and binder content. ANOVA calculation of proximate analyses showed complex influence of linear and nonlinear terms and the parameters were influenced by all variables.

The obtained results point out that olive pellets from cultivar 'Buža', presented the best quality when processed at 50 °C, without addition of binder (optimizing function gained its maximum value of 0.66). However, this analysis also showed that agro-pellets made from unconditioned material, with 2% addition of binder gave very good results (optimizing function gained values ranging from 0.63 -0.64), except for 'Buža' cultivar.

The produced pellets were mostly in boundaries proscribed by EU standards for fuel pellets, thus it can be concluded that they present good quality fuel. Conditioning treatment at 80 °C caused excessive rise of the moisture of the material, which consequently caused poorer quality of pellets. Problem may occur during combustion of olive cake pellets due to elevated nitrogen content in a form of high NO emissions.

SOP and ANN-based models were developed for prediction of C, H, N and S content, particle density, abrasion and length, and also moisture and ash content, HHV, LHV, fixed carbon and volatile matter content for a wide range of input variables. Both models are easy to implement and could be effectively used for predictive purposes, modelling and optimization. As compared to RSM, ANN model yielded a better fit of experimental data. Taking into account that a considerable amount and wide variety of data were used in the present work to obtain the ANN model, and considering that the model turned out to yield a sufficiently good representation of the experimental results, it can be expected that it will be useful in practice.

AKNOWLEDGEMENTS

This article is written within the projects III 46005 and TR-31055, 2011-2014, funded by the Serbian Ministry of Education, Science and Technological Development.

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Naučni rad

THE QUALITY ANALYSES OF OLIVE CAKE FUEL PELLETS - MATHEMATICAL APPROACH

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SAŽETAK

U ovom članku su ispitivani uticaja procesnih parametara (temperature kondicioniranja i sadržaj veziva), na kvalitet konačnog proizvoda, agro - peleta, koje se koriste za oslobađanje toplotne energije, dobijene od četiri različite vrste maslina, iskazan preko različitih tehnoloških parametara. Tehnološke, fizičke i hemijske osobine peleta (sadržaj ugljenika, vodonika , azota i sadržaj sumpora , zatim gustina čestica , dužine, habanje , vlage , sadržaja pepela , gornje i donje toplotne moći, sadržaj fiksnog ugljenika i sadržaj lako zapaljivih materija) su određeni da bi se izvršila procena njihovog kvaliteta . U radu je izvršeno poređenje performansi neuronske mreže (engl. Artificial Neural Network - ANN) sa razvijenim matematičkim modelom u obliku polinoma drugog reda (engl. Second Order Polynomial - SOP), kao i sa vrednostima dobijenim eksperimentalnim merenjima, u cilju dobijanja dovoljno tačnog i adekvatnog matematičkog modela za predviđanje parametara kvaliteta agro - peleta . SOP model je pokazao dobru tačnost, iskazanu visokim koeficijentima determinacije (R^2) ,koji su bili između 0.692 i 0.955, dok je ANN model pokazao visok stepen poklapanja sa eksperimentalnim merenjima, sa R^2 vrednostima između 0.544 i 0.994 .

Ključne reči: pogača masline; sorte masline; agro-pelete; peletiziranje; matematički model

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Figure 1. Comparison of experimentally obtained results with ANN predicted values of carbon, hydrogen, nitrogen and sulphur content, particle density, abrasion and length, and also moisture and ash content, higher heating value, fixed carbon and volatile matter content

Slika 1. Poređenje eksperimentalno dobijenih vrednosti sa rezultatima neuronske mreže, za predikciju ugljenika, azota i sumpora, gustine čestica, abrazije i dužine pelete, kao i vlažnosti i sadržaja pepela, gornje toplotne moći, količine fiksnog ugljenika i isparljive materije

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Table 1. Experimental design for each cultivar

	Conditioning	Binder
1	No conditioning	No binder
2		1 % binder
3		2 %binder
4	Conditioned at 50 °C	No binder
5		1 % binder
6		2 %binder
7	Conditioned at 80 °C	No binder
8		1 % binder
9		2 %binder

Table 2. Codes

Code	1	2	3	4
Cultivar name	'Istarska Bjelica'	‘Buža’	‘Leccino’	‘Pendolino’
Temperature (^{o}C)	0	50	80	-
Binder content (%)	0	1	2	-

Table 3. Ultimate analysis and physical properties of oil cake

Run No.	C	T (^{o}C)	B (%)	Ultimate analysis Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Physical properties Particle density (g/cm^3)	Abrasion	Length (mm)
1	1	1	1	54.37±0.16^{abc}	7.41±0.05^{bcd}	0.69±0.01^{a}	0.07±0.00^{d}	1.24±0.00^{efghijk}	15.92±0.01^{z}	11.24±0.04^{f}
2	1	1	2	54.62±0.08^{ab}	7.33±0.06^{bcd}	0.69±0.00^{ab}	0.07±0.00^{d}	1.23±0.01^{cdefghi}	15.92±0.04^{z}	11.16±0.06^{f}
3	1	1	3	53.53±0.42^{a}	7.37±0.05^{bcd}	0.70±0.00^{bcd}	0.07±0.00^{bcd}	1.26±0.01^{klmnop}	10.37±0.05^{r}	9.98±0.07^{e}
4	1	2	1	54.63±0.18^{abc}	7.34±0.02^{ab}	0.70±0.00^{ab}	0.07±0.00^{cd}	1.25±0.01^{efghijkl}	9.47±0.05^{q}	12.27±0.04^{hi}
5	1	2	2	54.52±0.27^{abc}	7.28±0.02^{ab}	0.71±0.01^{abc}	0.07±0.00^{bcd}	1.26±0.01^{ghijklmn}	9.22±0.02^{p}	12.71±0.04^{lm}
6	1	2	3	53.70±0.25^{a}	7.26±0.03^{a}	0.72±0.01^{d}	0.07±0.00^{abc}	1.27±0.01^{lmnopq}	8.97±0.02^{o}	11.84±0.06^{g}
7	1	3	1	54.67±0.24^{abc}	7.43±0.06^{cde}	0.69±0.00^{ab}	0.07±0.00^{abc}	1.20±0.00^{ab}	5.33±0.02^{hi}	12.42±0.11^{ijk}
8	1	3	2	54.31±0.35^{abc}	7.39±0.06^{abc}	0.70±0.00^{abc}	0.07±0.00^{ab}	1.22±0.01^{abc}	5.37±0.01^{ghi}	13.17±0.11^{p}
9	1	3	3	53.61±0.11^{a}	7.35±0.06^{abc}	0.72±0.00^{cd}	0.07±0.00^{a}	1.23±0.01^{cdefgh}	5.25±0.03^{fgh}	12.63±0.07^{klm}
10	2	1	1	56.60±0.47^{jklm}	8.07±0.03^{klmn}	1.03±0.00^{ijkl}	0.08±0.00^{mnopq}	1.25±0.01^{lmnopq}	15.22±0.09^{y}	7.18±0.01^{b}
11	2	1	2	57.06±0.02^{m}	8.09±0.01^{klmn}	1.06±0.01^{opq}	0.08±0.00^{r}	1.27±0.01^{nopqr}	14.20±0.12^{x}	6.43±0.02^{a}
12	2	1	3	56.83±0.41^{ijklm}	8.16±0.04^{no}	1.07±0.00^{pq}	0.08±0.00^{ijk}	1.29±0.01^{qrs}	13.90±0.10^{w}	6.45±0.04^{a}
13	2	2	1	56.72±0.38^{jklm}	8.18±0.03^{no}	1.04±0.01^{ghij}	0.08±0.00^{ef}	1.26±0.01^{ijklmno}	7.97±0.04^{n}	13.11±0.11^{o}
14	2	2	2	57.68±0.27^{lm}	8.19±0.07^{no}	1.06±0.01^{mnop}	0.08±0.00^{lmn}	1.28±0.00^{opqr}	7.14±0.04^{m}	13.08±0.10^{op}
15	2	2	3	57.38±0.31^{jklm}	8.21±0.03^{lmno}	1.06±0.00^{lmnop}	0.08±0.00^{ghij}	1.30±0.01^{rs}	6.89±0.04^{l}	12.48±0.06^{hij}
16	2	3	1	56.85±0.13^{ghijkl}	8.19±0.07^{mno}	1.07±0.00^{lmnop}	0.08±0.00^{e}	1.21±0.01^{a}	6.71±0.05^{k}	12.58±0.06^{ijk}
17	2	3	2	57.08±0.44^{jklm}	8.15±0. 07^{lmno}	1.07±0.01^{q}	0.08±0.00^{opqr}	1.23±0.00^{bcde}	5.47±0.03^{ij}	12.29±0.02^{h}
18	2	3	3	57.29±0.18^{klm}	8.08±0.05^{klm}	1.06±0.01^{opq}	0.08±0.00^{nopqr}	1.25±0.01^{fghijklm}	4.51±0.04^{d}	12.66±0.11^{lm}
19	3	1	1	56.36±0.13^{efghij}	7.63±0.02^{efg}	1.06±0.00^{mnop}	0.08±0.00^{kl}	1.26±0.00^{hijklmno}	11.26±0.06^{t}	7.24±0.06^{b}
20	3	1	2	55.87±0.20^{defghi}	7.63±0.04^{efg}	1.02±0.01^{fgh}	0.08±0.00^{fgh}	1.25±0.01^{hijklmno}	11.16±0.05^{t}	8.03±0.04^{d}
21	3	1	3	55.81±0.25^{efghij}	7.72±0.08^{ghi}	1.04±0.00^{ghijk}	0.08±0.00^{qr}	1.29±0.01^{pqrs}	10.42±0.09^{s}	8.20±0.06^{d}
22	3	2	1	56.40±0.31^{hijklm}	7.50±0.06^{def}	1.05±0.01^{jklmn}	0.08±0.00^{ghij}	1.27±0.01^{nopqr}	5.57±0.02^{j}	12.35±0.06^{ijk}
23	3	2	2	55.90±0.06^{efghij}	7.69±0.01^{efg}	1.01±0.00^{f}	0.08±0.00^{fgh}	1.27±0.01^{klmnop}	5.62±0.04^{j}	12.98±0.10^{o}
24	3	2	3	56.06±0.28^{efghij}	7.84±0.04^{ij}	1.03±0.01^{ghijk}	0.08±0.00^{pqr}	1.30±0.01^{s}	4.93±0.01^{e}	12.54±0.03^{jkl}
25	3	3	1	55.44±0.02^{cdefg}	7.70±0.04^{ghi}	1.05±0.01^{jklm}	0.08±0.00^{lmnop}	1.23±0.01^{defghi}	5.28±0.03^{ghi}	12.74±0.08^{lm}
26	3	3	2	54.87±0. 39^{bcdef}	7.95±0.04^{jk}	1.02±0.01^{fghi}	0.08±0.00^{klm}	1.22±0.00^{abcd}	5.13±0.03^{f}	12.42±0.05^{ijk}
27	3	3	3	55.41±0.59^{bcde}	8.20±0.04^{no}	1.06±0.00^{nop}	0.09±0.00^{s}	1.26±0.01^{mnopqr}	4.24±0.01^{c}	12.74±0.04^{lm}
28	4	1	1	54.26±0.49^{abc}	7.37±0.04^{bcd}	0.89±0.00^{e}	0.07±0.00^{a}	1.23±0.01^{bcde}	13.47±0.13^{v}	7.13±0.01^{b}
29	4	1	2	55.77±0.16^{defghi}	7.68±0.06^{gh}	1.02±0.00^{fg}	0.08±0.00^{fghi}	1.23±0.01^{defghij}	12.79±0.06^{u}	7.48±0.04^{c}
30	4	1	3	56.12±0.37^{defghi}	7.74±0.03^{ghi}	1.04±0.01^{ghijk}	0.08±0.00^{opqr}	1.26±0.01^{mnopqr}	9.40±0.04^{pq}	8.15±0.03^{d}
31	4	2	1	56.06±0.26^{fghijk}	7.53±0.03^{def}	1.05±0.01^{klmno}	0.08±0.00^{hij}	1.26±0.01^{jklmnop}	5.20±0.00^{fg}	12.04±0.01^{g}
32	4	2	2	55.94±0.38^{defgh}	7.63±0.01^{fg}	1.01±0.00^{fgh}	0.08±0.00^{efg}	1.24±0.01^{efghijk}	5.15±0.04^{f}	13.15±0.09^{op}
33	4	2	3	56.10±0.09^{efghij}	7.84±0.04^{hij}	1.04±0.01^{hijk}	0.08±0.00^{nopqr}	1.29±0.01^{rs}	4.49±0.01^{d}	12.45±0.11^{ijk}
34	4	3	1	55.54±0.19^{cdefgh}	7.72±0.05^{fg}	1.05±0.01^{jklmn}	0.08±0.00^{lmno}	1.23±0.01^{bcdefg}	4.42±0.02^{d}	12.76±0.06^{mn}
35	4	3	2	55.37±0.08^{abcd}	8.02±0.07^{jkl}	1.03±0.01^{ghij}	0.08±0.00^{jkl}	1.22±0.00^{bcdef}	3.68±0.02^{b}	13.00±0.07^{no}
36	4	3	3	55.54±0.25^{cdef}	8.22±0.02^{o}	1.06±0.01^{mnop}	0.09±0.00^{s}	1.26±0.01^{mnopqr}	3.43±0.02^{a}	13.17±0.05^{p}
Polarity				+	+	-	-	+	-	Opt. <30 mm

The results are presented as mean±SD; Different letter within the same row indicate significant differences ($p < 0.05$), according to Tukey's test. Polarity: '+' = the higher the better criteria, '−' = the lower the better criteria, C - cultivar type, T - temperature, B - binder content code

Table 4. Proximate analysis of oil cake

Run No.	Moisture (%)	Ash	HHV (MJ/kg)	LHV (MJ/kg)	Fixed carbon (%)	Volatile matter (%)
1	7.18±0.01^{bc}	1.92±0.01^{gh}	22.33±0.06^{abc}	20.84±0.22^{ab}	16.43±0.06^{gh}	80.82±0.3 ^{gh}
2	7.02±0.05^{b}	1.93±0.01^{h}	22.41±0.08^{abc}	20.86±0.14^{ab}	16.13±0.12^{fg}	80.65±0. 46^{efgh}
3	7.09±0.04^{bc}	1.95±0.01^{gh}	22.44±0.16^{abc}	20.81±0.07^{ab}	17.68±0.05^{mn}	78.71±0.39^{bcdef}
4	9.34±0.05^{f}	1.94±0.01^{gh}	22.41±0.11^{abc}	20.88±0.13^{ab}	16.28±0.13^{gh}	80.69±0.40^{efgh}
5	9.34±0.03^{f}	1.92±0.01^{h}	22.30±0.07^{ab}	20.81±0.15^{ab}	15.90±0.05^{f}	80.53±0.38^{fgh}
6	9.31±0.09^{f}	1.93±0.02^{gh}	22.39±0.15^{abc}	20.67±0.07^{ab}	17.21±0.08^{l}	79.48±0.53^{cdefgh}
7	12.42±0.11^{i}	1.90±0.00^{gh}	22.36±0.21^{abc}	20.72±0.06^{ab}	16.06±0.00^{fg}	80.77±0.31^{efgh}
8	12.60±0.10^{i}	1.90±0.01^{efg}	22.41±0.04^{abc}	20.85±0.06^{ab}	15.40±0.08^{e}	81.43±0.71^{h}
9	12.40±0.09^{i}	1.89±0.01^{fgh}	22.44±0.14^{a}	20.75±0.08^{ab}	16.41±0.03^{ghi}	80.14±0.40^{cdefgh}
10	6.15±0.03^{a}	1.56±0.01^{a}	22.62±0.14^{abc}	20.92±0.03^{ab}	16.37±0.14^{ghi}	80.55±0.21^{h}
11	6.17±0.03^{a}	1.56±0.00^{a}	22.51±0.15^{abc}	20.93±0.19^{ab}	16.65±0.13^{ijk}	80.26±0.64^{defgh}
12	6.16±0.02^{a}	1.56±0.01^{a}	22.49±0.10^{abc}	20.73±0.20^{ab}	17.54±0.08^{lm}	79.49±0.47^{bcde}
13	9.30±0.05^{f}	1.56±0.01^{a}	22.76±0.18^{abc}	20.98±0.01^{ab}	16.93±0.09^{jk}	79.35±0.20^{cdefgh}
14	9.37±0.09^{f}	1.55±0.01^{a}	22.59±0.11^{abc}	20.94±0.12^{ab}	16.87±0.03^{jk}	80.18±0.29^{cdefgh}
15	9.30±0.02^{f}	1.56±0.01^{a}	22.57±0.17^{abc}	20.81±0.08^{ab}	17.56±0.15^{lm}	78.85±0.42^{cdef}
16	11.16±0.11^{g}	1.56±0.01^{a}	22.73±0.06^{bc}	20.79±0.07^{ab}	16.90±0.02^{k}	79.39±0.23^{cdefgh}
17	11.18±0.06^{g}	1.54±0.00^{a}	22.64±0.07^{abc}	20.91±0.16^{ab}	16.55±0.11^{hij}	79.68±0.61^{cdefg}
18	11.09±0.03^{g}	1.56±0.01^{a}	22.66±0.04^{abc}	20.90±0.12^{ab}	16.86±0.07^{k}	79.41±0.78^{bc}
19	7.22±0.06^{bc}	1.87±0.01^{de}	22.63±0.17^{abc}	20.88±0.15^{ab}	12.97±0.04^{d}	83.96±0.39^{i}
20	7.21±0.06^{c}	1.86±0.02^{de}	22.46±0.05^{abc}	20.85±0.01^{ab}	18.89±0.08^{o}	77.88±0.02^{ab}
21	7.16±0.06^{bc}	1.83±0.02^{bc}	22.55±0.07^{abc}	21.02±0.14^{ab}	19.04±0.15^{p}	77.32±0.46^{a}
22	8.94±0.07^{e}	1.86±0.01^{d}	22.53±0.16^{bc}	20.94±0.04^{b}	5.45±0.03^{a}	92.33±0.18^{j}
23	8.80±0.08^{e}	1.87±0.01^{def}	22.57±0.14^{abc}	20.97±0.18^{ab}	11.54±0.08^{b}	84.90±0.50^{i}
24	8.86±0.06^{e}	1.85±0.01^{bcd}	22.48±0.02^{abc}	20.73±0.11^{ab}	12.26±0.08^{c}	84.47±0.12^{i}
25	10.96±0.08^{g}	1.84±0.01^{bcd}	22.52±0.10^{abc}	20.85±0.12^{ab}	11.38±0.08^{b}	85.15±0.41^{i}
26	10.96±0.04^{g}	1.85±0.01^{d}	22.57±0.07^{abc}	20.74±0.19^{ab}	17.88±0.00^{n}	78.65±0.27^{bc}
27	11.00±0.05^{g}	1.85±0.02^{bcd}	22.35±0.17^{abc}	20.79±0.05^{ab}	19.02±0.15^{op}	77.32±0.71^{a}
28	7.08±0.05^{bc}	1.85±0.00^{bcd}	22.46±0.11^{abc}	20.88±0.16^{b}	16.34±0.00^{ghi}	80.53±0.09^{efgh}
29	7.10±0.07^{b}	1.86±0.01^{de}	22.60±0.02^{c}	20.86±0.17^{ab}	18.69±0.10^{o}	80.62±0.28^{gh}
30	7.03±0.02^{b}	1.84±0.01^{b}	22.56±0.15^{abc}	20.89±0.09^{ab}	19.14±0.10^{p}	81.16±0.46^{h}
31	8.19±0.02^{d}	1.86±0.01^{de}	22.52±0.06^{abc}	20.93±0.12^{ab}	5.43±0.04^{a}	80.23±0.44^{fgh}
32	8.17±0.04^{d}	1.86±0.01^{def}	22.73±0.03^{bc}	20.95±0.03^{ab}	11.55±0.02^{b}	81.36±0.58^{h}
33	8.18±0.06^{d}	1.85±0.01^{d}	22.56±0.18^{abc}	20.87±0.12^{ab}	12.15±0.09^{c}	80.96±0.15^{efgh}
34	12.04±0.09^{h}	1.84±0.01^{bcd}	22.52±0.14^{abc}	20.86±0.09^{ab}	11.37±0.10^{b}	78.58±0.74^{bc}
35	11.98±0.06^{h}	1.85±0.02^{cd}	22.39±0.13^{abc}	20.85±0.07^{ab}	18.00±0.14^{n}	79.14±0.58^{bcd}
36	11.93±0.02^{h}	1.85±0.02^{bcd}	22.49±0.10^{abc}	20.67±0.12^{a}	18.94±0.10^{op}	80.18±0.69 ^{cdefgh}
Polarity	0pt. <10%	-	+	+	+	+

The results are presented as mean±SD; Different letter within the same row indicate significant differences ($p < 0.05$), according to Tukey’s test. Polarity: ‘+’ = the higher the better criteria, ‘−’ = the lower the better criteria.

Table 5. ANOVA table (sum of squares for each assay)

	dF	Particle density	Abrasion	Length	Moisture	Ash	Carbon	H	N	S	HHV	LHV	Fixed carbon	Volatile matter
C	1	0.00*	135.22*	7.37*	2.99*	0.01*	8.21*	0.93*	1.16*	0.00*	0.18*	0.01**	83.86*	8.38**
C^2	1	0.01*	0.17	10.85*	4.62*	0.87*	59.67*	4.12*	0.94*	0.00*	0.09*	0.00	0.07	20.76*
T	1	0.01*	1132.59*	363.28*	404.35*	0.00	1.20*	0.46*	0.01**	0.00*	0.06*	0.10*	16.03**	1.99
T^2	1	0.01*	109.95*	106.29*	2.10*	0.00	2.80*	0.14**	0.00	0.00*	0.00	0.00	286.33*	97.48*
B	1	0.02*	44.91*	0.01	0.02	0.00	0.01	0.42*	0.01**	0.00*	0.17*	0.06*	220.98*	94.37*
B^2	1	0.00*	3.32	1.36	0.00	0.00	0.24	0.00	0.00	0.00	0.00	0.02**	19.05**	6.99**
C × T	1	0.00*	5.79*	18.97*	1.42*	0.00	0.34	0.42*	0.01**	0.00*	0.01**	0.06*	4.14	3.08**
C × B	1	0.00	0.26	4.13*	0.00	0.00	0.86**	0.69*	0.00	0.00*	0.01**	0.04*	98.21*	1.23
T × B	1	0.00	9.87*	0.16	0.00	0.00	0.12	0.01	0.00	0.00	0.01**	0.00	3.25	0.14
Error	98	0.01	108.28	57.27	19.60	1.23	48.43	3.61	0.26	0.00	0.74	0.58	498.23	4.18
r^2		0.841	0.930	0.899	0.955	0.719	0.753	0.765	0.892	0.845	0.736	0.697	0.774	0.692

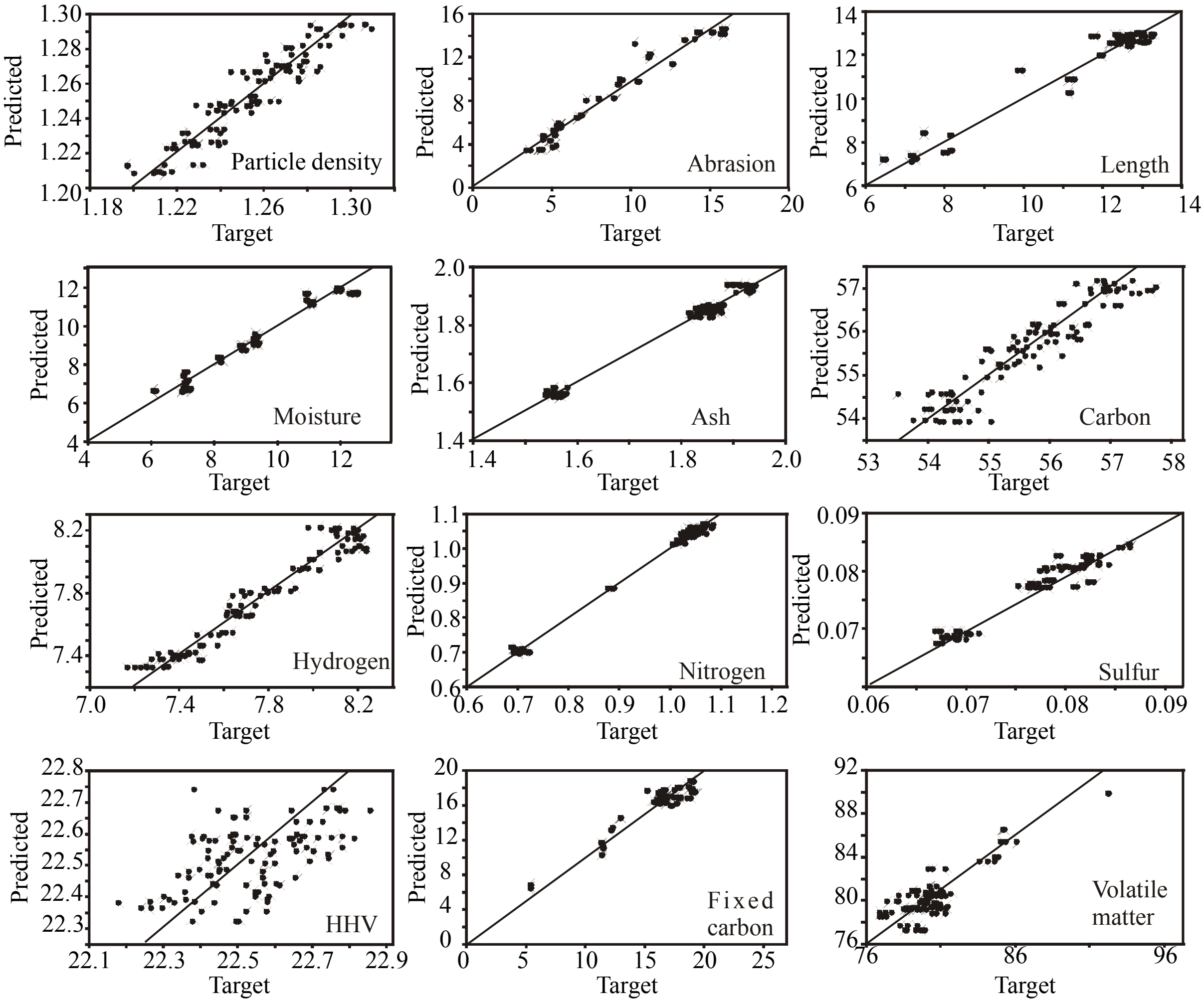
*Significant at $p<0.05$ level, **Significant at $p<0.10$ level, 95% confidence limit, error terms have been found statistically insignificant, C-cultivar, T-temperature, B-binder. dF - degrees of freedom.

Table 6. Performance of the optimal ANN

Cycle	Particle density	Abr.	Length	Moisture	Ash	Carbon	H	N	S	HHV	LHV	Fixed carbon	Volatile matter
Train.	0.941	0.981	0.980	0.983	0.994	0.951	0.965	0.997	0.960	0.672	0.544	0.967	0.914
Test.	0.934	0.980	0.985	0.981	0.988	0.932	0.981	0.997	0.968	0.504	0.431	0.962	0.883
Valid.	0.953	0.949	0.959	0.973	0.989	0.907	0.977	0.997	0.965	0.247	0.118	0.929	0.828

Table 7. Mean and standard deviation of the residuals for the optimal ANN

	Particle density	Abr.	Length	Moisture	Ash	Carbon	H	N	S	HHV	LHV	Fixed carbon	Volatile matter
Mean	0.001	0.125	-0.081	0.022	-0.002	0.068	-0.002	0.001	0.000	0.015	-0.009	-0.036	0.158
SD	0.009	0.859	0.483	0.400	0.018	0.381	0.078	0.012	0.002	0.125	0.120	0.991	1.238



Particle density
Abrasion
Length
Moisture
Ash
Carbon
Hydrogen
Nitrogen
Sulfur
HHV
Fixed carbon
Volatile matter
Predicted
Target

Figure 1.

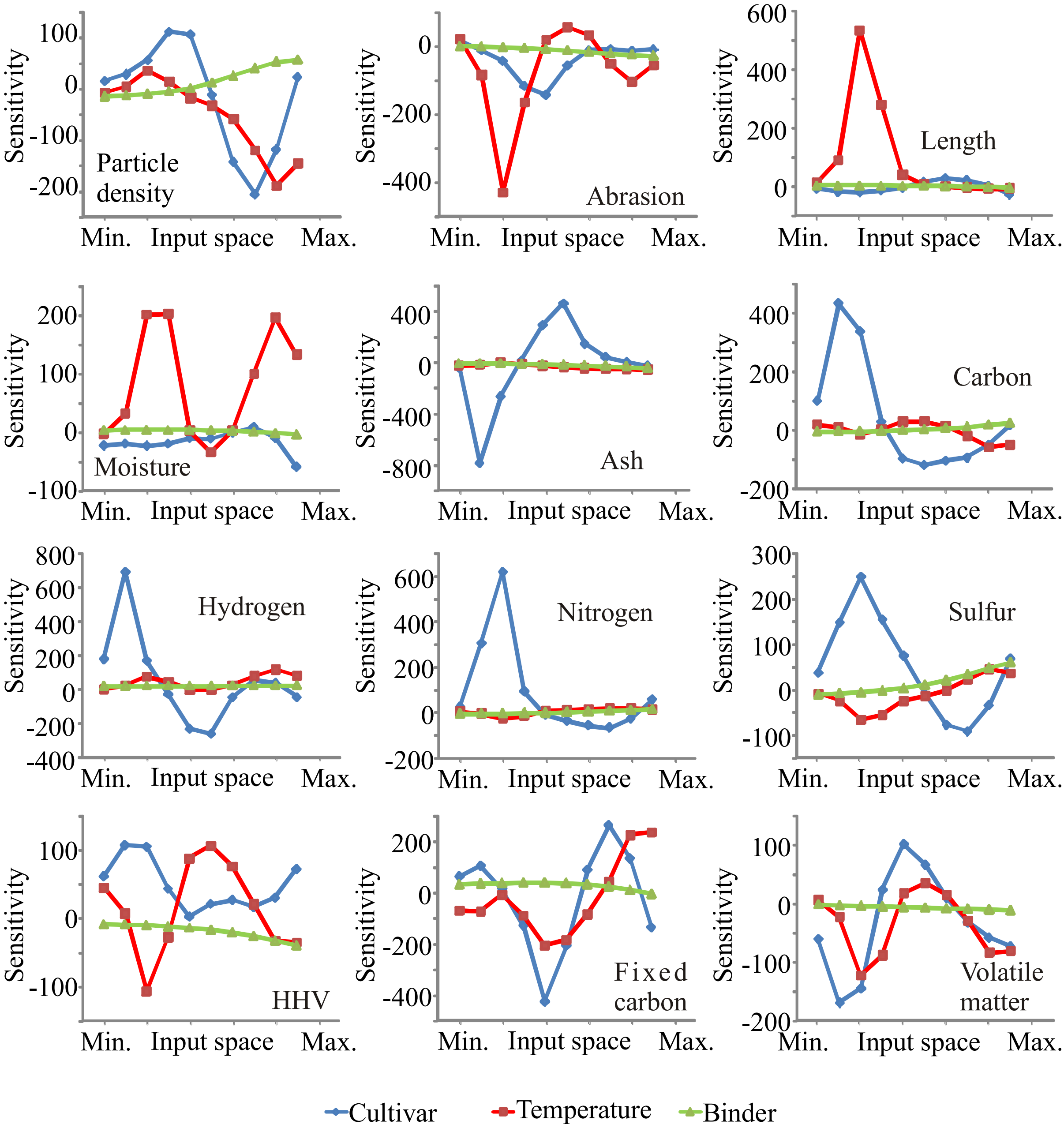
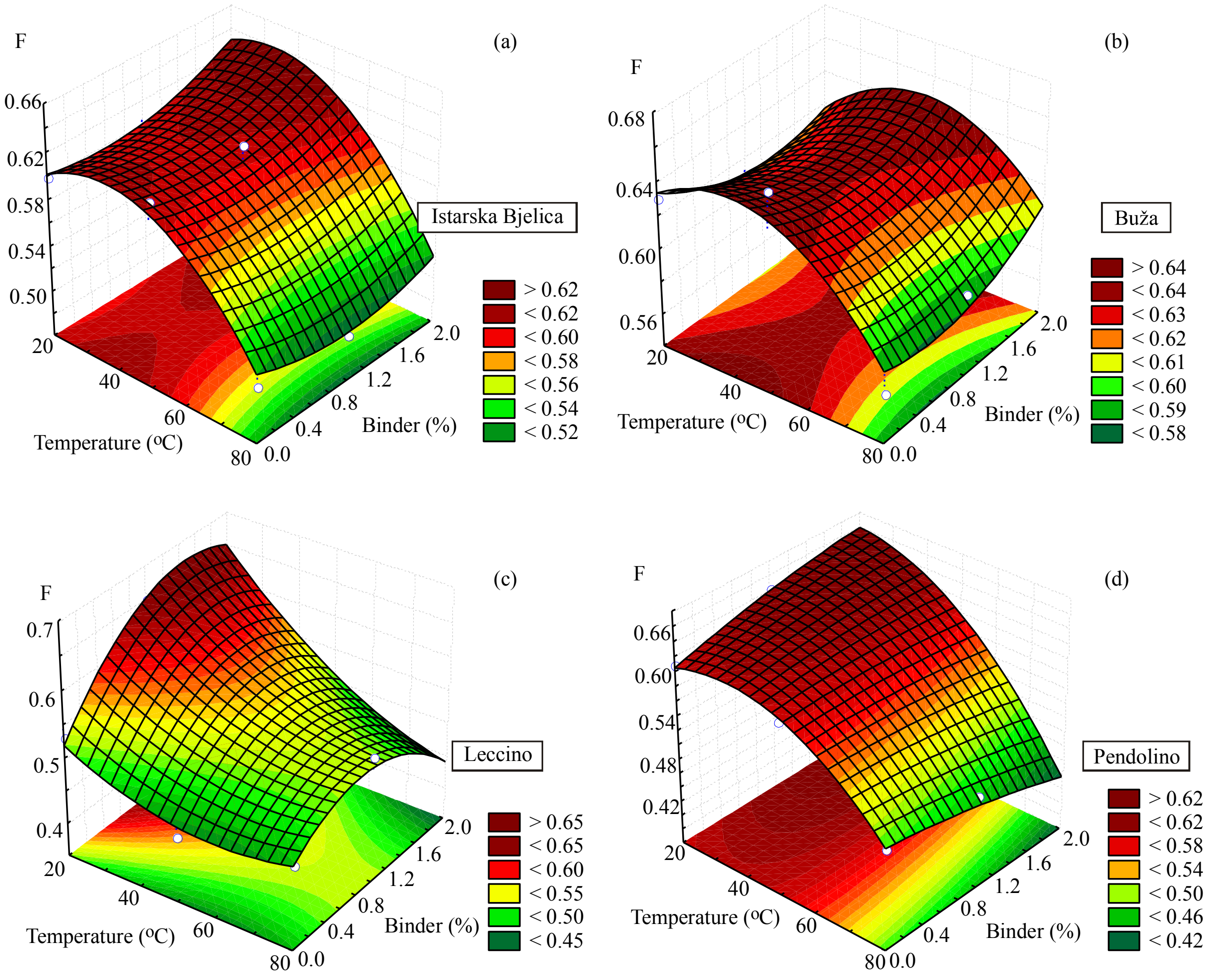

Particle density
Abrasion
Length
Moisture
Ash
Carbon
Hydrogen
Nitrogen
Sulfur
HHV
Fixed carbon
Volatile matter
Sensitivity
Min.
Input space
Max.
Cultivar
Temperature
Binder

Figure 2.



F
(a)
0.66
0.62
0.58
0.54
0.50
Istarska Bjelica
> 0.62
< 0.62
< 0.60
< 0.58
< 0.56
< 0.54
< 0.52
20
40
60
80
Temperature (ºC)
0.0
0.4
0.8
1.2
1.6
2.0
Binder (%)
F
(b)
0.68
0.64
0.60
0.56
Buža
> 0.64
< 0.64
< 0.63
< 0.62
< 0.61
< 0.60
< 0.59
< 0.58
20
40
60
80
Temperature (ºC)
0.0
0.4
0.8
1.2
1.6
2.0
Binder (%)
F
(c)
0.7
0.6
0.5
0.4
Leccino
> 0.65
< 0.65
< 0.60
< 0.55
< 0.50
< 0.45
20
40
60
80
Temperature (ºC)
0.0
0.4
0.8
1.2
1.6
2.0
Binder (%)
F
(d)
0.66
0.60
0.54
0.48
0.42
Pendolino
> 0.62
< 0.62
< 0.58
< 0.54
< 0.50
< 0.46
< 0.42
20
40
60
80
Temperature (ºC)
0.0
0.4
0.8
1.2
1.6
2.0
Binder (%)

Figure 3.