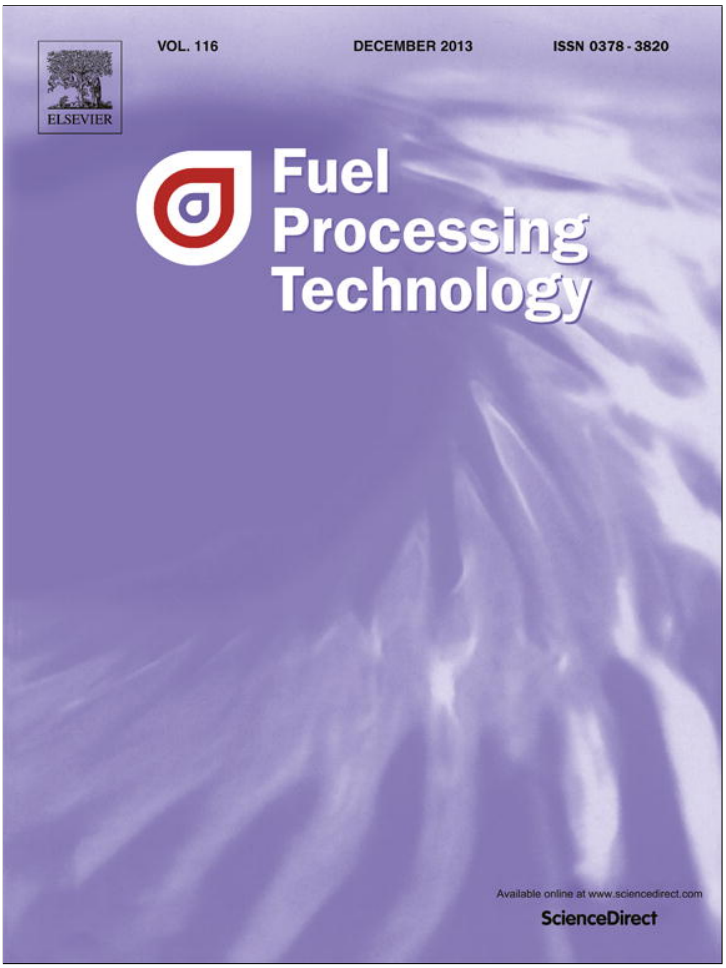
Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/authorsrights

Author's personal copy

Fuel Processing Technology 116 (2013) 250–256

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Chemometric approach for assessing the quality of olive cake pellets

Tea Brlek [a,*], Lato Pezo [b], Neven Voća [c], Tajana Krička [c], Đuro Vukmirović [a], Radmilo Čolović [a], Marija Bodroža-Solarov [a]

[a] Institute of Food Technology Novi Sad, University of Novi Sad, Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia
[b] Institute of General and Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11000 Beograd, Serbia
[c] Faculty of Agriculture, University of Zagreb, Svetosimunska 25, 10000 Zagreb, Croatia

ARTICLE INFO

Article history:
Received 13 May 2013
Received in revised form 25 June 2013
Accepted 9 July 2013
Available online 10 August 2013

Keywords:
Olive cake
Olive cultivar
Fuel pellets
Agro-pellets

ABSTRACT

This article investigates the influence of processing parameters (conditioning and binder content), on quality of fuel agro-pellets produced from four olive cultivars (Istarska Bjelica, Buža, Pendolino, Leccino) grown in experimental filed in Croatia (Istria). Physical and chemical properties of pellets have been determined to assess their quality. Low ash and sulphur levels were detected, with elevated nitrogen levels for all samples. Analysis of variance and post-hoc Tukey's HSD test at 95% confidence limit have been utilised to show significant differences between various samples. Low coefficients of variation have been obtained for each applied assay (0.09–2.98%), which confirmed the high accuracy of the measurements. Score analysis and principal component analysis have been used for assessing the effect of process variables and variety of cultivars on final quality of pellets. For PCA modelling, experimental data for physical and chemical properties have been used. Standard score analysis revealed that equally good physical and chemical characteristics of pellets can be obtained with conditioning at 50 °C, but also without conditioning. The use of binders didn't affect the quality of pellets as much.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Olive oil production, as one of the most important branches of Croatian agriculture and other Mediterranean countries, results in vast amounts of organic residues, with fresh olive cake as the main by-product. Estimated quantity of residues generated in the production of olive oil in the EU is around 6.8 million tonnes per year [1], while Croatia produces slightly less than 40 000 tonnes of olives per year [2], out of which approximately 16 000 tonnes of fresh cake is produced. Olive cake consists of solids and a part of vegetable water, and its consistency is similar to a paste. Such material is difficult to manipulate and it dries slowly, therefore many problems occur by its disposal [3].

Due to high amount of waste that olive oil production generates, it would be useful to find an environmentally friendly way of its utilisation. One of the methods of olive cake utilisation is production of thermal energy by combustion. The main technical and technological problem of combustion of olive cake is the low energy value per unit mass. Additionally, olive cake requires large storage spaces. The simplest way to enable more efficient usage of this residue as a source of energy is to process it by pelletization process.

Various factors can affect the quality of the pelleted product, such as moisture content, particle size and shape, chemical composition of raw material, and type of processing equipment. Agricultural residues, due to their low bulk density and specific chemical composition are hard to compress, while wood residues, such as sawdust and wood chips, have a structure with good compression properties and contain natural binders, such as lignin. Thus, the addition of material containing these natural binders or addition of commercial binders can improve the quality of pellets [4].

Conditioning of the material before pelletization by addition of steam or water may also improve pellet quality as this pre-treatment affects moisture content of the material. Conditioning is usually done by adding saturated steam at a given pressure, which increases the temperature and moisture of the material. Higher moisture content of the material reduces the energy consumption during pelletization [5], as well as lowers the friction in pellet press which affects pellet quality and the pelletization process itself [6,7]. The application of steam to prepare material for pelletization is used to obtain higher quality pellets [8,9]. Addition of heat and moisture affects the components in the material, such as starch and protein, activating their binding properties [10]. However, the application of too much heat or water can reduce the production capacity and quality of pellets [7].

Agro-pellets from olive cake are a product of uniform shape and size, which is much easier to manipulate than the starting material. Namely, pelletization facilitates transport (easier material handling, reducing transport costs), storage (reducing storage space), feeding

* Corresponding author. Tel.: +381 61 356 0193.
E-mail addresses: tea.brlek@fins.uns.ac.rs (T. Brlek), latopezo@yahoo.co.uk (L. Pezo), nvoca@agr.hr (N. Voća), tkricka@agr.hr (T. Krička), djuro.vukmirovic@fins.uns.ac.rs (Đ. Vukmirović), radmilo.colovic@fins.uns.ac.rs (R. Čolović), marija.bodroza@fins.uns.ac.rs (M. Bodroža-Solarov).

0378-3820/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.fuproc.2013.07.006

Author's personal copy

in to combustion furnace and burnout. Also, it is important that pelletization increases the heating value per unit mass of cake [10,11].

Olive cake was previously investigated as a potential bio-fuel, where its chemical composition and characteristics for energy utilisation have been analysed, as well as the combustion of this residue. It has been proven that the use of olive cake as fuel significantly reduces the emissions of sulphur oxide, which is very high when burning fuel oil [12] and that it is a good energy source for the production of "clean" energy, considering that all of flue gas emissions were lower than recommended by EU directives on emissions of pollutants from large burning facilities [13].

It is shown that different fractions of waste from the production of olive oil have different combustion characteristics. Olive cake together with olive kernel emerged as the best fuel, with the smallest proportion of unburnt residue and maximum combustion efficiency [14].

Olive cake can be pelletized in combination with other materials. Thermal decomposition of pellets made of olive cake in combination with wood biomass depends primarily on the chemical composition of the samples, i.e. on ratio olive cake/wood biomass. With increase of share of olive cake in pellets, emissions of nitric oxide (NO) and sulphur dioxide (SO_2) also increase, which is understandable because the cake has more sulphur and nitrogen, than wood biomass [15].

In comparison with wood biomass pellets made from olive cake have higher calorific value. Olive cake pellets have low sulphur content, but higher ash and nitrogen content. Pellets made from olive cake can be considered to have acceptable properties for thermal utilisation. However there are restrictions for content of ash and nitrogen, which can lead to problems during combustion in the furnace. Physical properties of olive cake pellets can be improved by addition of wood biomass [16].

The objective of this study was to investigate the quality of pellets made from different cultivars of olive cake with and without addition of binder and with or without conditioning of the starting material. To assess the quality of pellets their physical and chemical characteristics have been determined. Experimental results have been subjected to analysis of variance (ANOVA) to show relations between applied assays (physical and chemical). In order to enable more comprehensive comparison between investigated samples, standard score (SS) has been introduced. Principal component analysis (PCA) has been applied to classify and discriminate analysed samples.

2. Materials and methods

2.1. Material

Four olive cake cultivars have been used in the research: Buža, Leccino, Pendolino and Istarska Bjelica grown in an ameliorated experimental field near Novigrad, Istria, Croatia. Olive cake was obtained after oil extraction from the fruit intended for the production of extra virgin olive oil from an olive oil mill in Istria in Novigrad, Croatia. The olive cake was a product after three way extraction method. The chemical composition of obtained cake was analysed, and the results were published in a previous investigation [17] and are presented in Table 1.

2.2. Preparation of the material

Olive cake obtained from the mill had an average moisture content of 50%, so it was dried at 40 °C in a biomass dryer until it reached 12%, which is optimal for storage and pelletization.

The cake was then milled using a laboratory hammer mill ("ABC Engineering", Pancevo, Serbia) where a sieve with a mesh size of 4 mm was used. Hammer mill was used to increase specific surface area of the material particles thus making the pelletization easier, because larger surface area of particles per unit volume is available for absorption of water and condensed steam during the process of conditioning. Grinding also improves the quality of the pellets due better packing of particles and reduction of gaps between them, so there are fewer weak points in pellets.

Table 1
Chemical composition of olive cake.

%, dry basis	I. Bjelica	Buža	Leccino	Pendolino
pH	4.47 ± 0.02^{d}	7.07 ± 0.06^{a}	6.24 ± 0.23^{b}	5.13 ± 0.02^{c}
Protein	6.17 ± 0.10^{b}	4.39 ± 0.10^{c}	6.68 ± 0.10^{a}	6.61 ± 0.19^{a}
Raw cellulose	40.09 ± 0.08^{a}	40.34 ± 0.03^{a}	40.72 ± 0.04^{a}	38.91 ± 0.04^{a}
Oil	6.28 ± 0.02^{b}	9.74 ± 0.04^{a}	4.58 ± 0.07^{c}	4.50 ± 0.02^{c}
Ash	1.84 ± 0.01^{b}	2.07 ± 0.07^{a}	1.56 ± 0.02^{c}	1.60 ± 0.03^{c}
C	55.54 ± 0.72^{a}	54.21 ± 0.63^{b}	56.64 ± 0.56^{a}	55.19 ± 0.77^{a}
H	7.38 ± 0.34^{b}	7.52 ± 0.24^{b}	8.10 ± 0.08^{a}	7.79 ± 0.27^{b}
N	0.99 ± 0.02^{b}	0.70 ± 0.02^{c}	1.07 ± 0.02^{a}	1.06 ± 0.03^{a}
S	0.069 ± 0.01^{b}	0.068 ± 0.01^{b}	0.083 ± 0.01^{a}	0.084 ± 0.01^{a}

The results are presented as mean ± SD; different letters within the same row indicate significant differences ($p < 0.05$), according to Tukey's test.

Olive cake can be pelletized with the addition of binders (as prescribed by DIN standard 51 731 to a maximum of 2%). In order to determine the least amount of binder without negative influence on pellet quality, material was pelletized without binder and with addition of binder in an amount of 1 and 2%. Lignocelluloses material was used as a binder in order to avoid introduction of any inorganic components to biomass pellets.

Material was used as unconditioned or it was conditioned by addition of steam. Steam conditioning was carried out in two-shaft paddle conditioner/mixer (SLHSJ0.2, Muyang Group, China) where steam was added directly into the material at a pressure of 2 bars, to achieve the desired temperature of 50 and 80 °C, respectively. Material was held in the conditioner/mixer until it reached the desired temperature, and afterwards was released into the heat insulated receiving hopper below the mixer. Time necessary to achieve desired temperatures was approximately 45 and 60 s, respectively.

The combination of the parameters: conditioning and addition of binder resulted in nine combinations of materials for each olive cake cultivar, which makes a total of 36 combinations for pelletization (shown in Table 2).

2.3. Pelletization of the olive cake

Prepared olive cake was pelletized in vertical pellet press (Pellet Press 14-175; Amandus Kahl) using die with a diameter of die openings of 6 mm and a thickness of 24 mm. Temperature of the die during pelletization ranged from 70 to 75 °C, and the throughput was 20 kg/h.

The pellets were cooled in vibrating drier/cooler (model FB 500 × 200, "Amandus Kahl", Germany), for 10 min at air temperature of 20 °C and the material flow of 18 kg/h.

2.4. Chemical analyses

Proximate analyses on the samples were done: moisture content [18], ash content [19], volatile mater [20] and fixed carbon (calculated by the difference between 100 and the sum of volatile matter, ash and moisture). Ultimate analyses done on the samples were: content of C,

Table 2
Combination of material.

	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

Author's personal copy

H, N [21] and S [22], higher heating value (HHV) and lower heating value (LHV) [23].

2.5. Physical analyses

Abrasion was determined with "Pfost" abrasion test device, Bühler, Switzerland. Two 500 g samples of pellets, separated from fine particles by using the sieve with a mash size of 4.8 mm (0.8 × pellet diameter), were subjected to abrasion action in two rotating boxes at 50 rpm. After 10 min, pellets were sieved using the same sieve and the amount of fine particles was determined and expressed as a percentage.

Density was determined by the hydrostatic method using analytical balance, with ethanol as a medium for wetting. Glass cup filled with liquid ethanol was placed on platform of the balance. The sample is placed in a cage that is fixed to a vertical bracket that has no physical contact with the glass. The difference in weight between the empty system and the sample in the cage allows the determination of the volume of the sample and density calculation using the formula [24]:

$$\rho_u = (m_u > e)e$$

where ρ_u is the density of the sample, m_u is the sample mass, m_e is the mass of ethanol, and ρ_e is the density of ethanol at a certain temperature.

Length of the pellets was measured by calliper.

2.6. Statistical analyses

Descriptive statistical analyses for all the obtained results have been expressed by means, standard deviation (SD), variance, and minimums and maximums, for each olive cultivar. 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. Furthermore, principal component analysis (PCA) has been applied successfully to classify and discriminate the different cultivars of olive. Pattern recognition technique has been applied within result descriptors to characterize and differentiate all varieties of olive cakes. The evaluation of one-way ANOVA and PCA of the obtained results has been performed using StatSoft Statistica 10.0® software [25].

2.7. Determination of normalized standard scores (SS)

In order to get a more complex observation of the ranking of olive cake quality, standard scores (SS) are evaluated using chemometric approach by integrating the measured values generated from different physical and chemical quality evaluation methods.

Min–max normalization is one of the most widely used technique to compare various characteristics of complex samples determined using multiple measurements, where samples are ranked based on the ratio of raw data and extreme values of the measurement used [26,27]. Since the units and the scale of the data from various physical and chemical characteristics are different, the data in each data set should be transformed into normalized scores, dimensionless quantity derived by subtracting the minimum value from the raw data, and divided by the subtract of maximum and minimum value, according to following 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.

Normalized scores of the most of physical and chemical properties are evaluated using above written equations, except for moisture and length parameters, which are evaluated according to optimal values, using trapezoidal function, as follows:

$$\bar{x}_i = \begin{cases} \min_i x_i \le x_i < m, & \dfrac{x_i - \min_i x_i}{m - \min_i x_i} \\ m \le x_i < n, & 1 \\ n \le x_i < \max_i x_i, & 1 - \dfrac{x_i - n}{\max_i x_i - n} \end{cases}, \quad \forall i, \text{ in case of "optimal range"criteria.}$$

where m and n are minimum and maximum of optimal range values (written in Tables 4, 5 and 6).

The sum of normalized scores of a sample for different measurements when averaged give a single unitless value termed as SS, which is a specific combination of data from different measuring methods with no unit limitation. This approach also enables the ease of employing some other set of olive cakes to this elaboration in the future comparisons.

Standard scores for integrated physical and chemical qualities for olive cakes are calculated and the results have been written to Table 8.

3. Results and discussion

3.1. ANOVA analyses with post-hoc Tukey's HSD

Each of the process variables has been coded, as shown in Table 3, and these codes are used for easier representation of experimental data.

Analysis of variance (Table 7) and the following post-hoc Tukey's HSD test have been evaluated for comparison of chemical and physical parameters. Statistically significant differences have been found in most cases, and the most influential variable was cultivar type, as expected. The influence of conditioning temperature is also observed, found statistically significant at $p < 0.05$ level. The impact of binder is far less important than these two factors, but still statistically significant.

Ultimate analyses (C, H, N and S contents) of four different olive cake cultivars (I. Bjelica, Buža, Leccino and Pendolino) are presented in Table 4 and the ANOVA calculation of these parameters in Table 7. The most important chemical parameters are contents of nitrogen and sulphur as these elements can cause environmental pollution when forming NO_x and SO_2 during pellet combustion. The levels of nitrogen were somewhat higher (0.96–1.07%) than for example in wood pellets, but still below levels in previous investigation, where Miranda et al. [16] found 1.98% of nitrogen in olive cake pellets. The differences are logical given that the cultivar influences the proportion of nitrogen, and in most studies it is not specified on which cultivar is the investigation done. Cultivars I. Bjelica and Buža had, on average, the lowest nitrogen content. On the other hand, levels of sulphur were found to be very low, i.e. below 0.1%, which is less than in wood pellets [28], and similar to the grape pomace pellets [29]. From this point of view, there could be some limitations during combustion of pellets regarding nitrogen oxide emissions.

Carbon levels proved to be higher than in some other agricultural residues, such as grape pomace [29] as well as in wood [28]. Higher carbon content in the fuel contributes to higher emissions of carbon oxides. Nevertheless, biomass during its growth adopts a large part of carbon dioxide, so this release during its combustion does not contribute to environmental pollution such as burning fossil fuels. In addition

Table 3
Coded variables.

Code	1	2	3	4
Cultivar	I. Bjelica	Buža	Leccino	Pendolino
Conditioning temp. (°C)	Without	50	80	–
Binder (%)	0	1	2	–

Author's personal copy

Table 4
Ultimate analysis of pellets.

Cultivar	Descriptive statistics	C (%)	H (%)	N (%)	S (%)
1	Mean	54.30	7.35	0.70	0.07
	SD	1.41	0.21	0.03	0.00
	Variance	1.98	0.04	0.00	0.00
	Min.	52.05	6.99	0.65	0.06
	Max.	57.84	7.88	0.77	0.08
2	Mean	54.30	7.35	0.70	0.07
	SD	0.65	0.33	0.06	0.01
	Variance	0.43	0.11	0.00	0.00
	Min.	55.87	7.61	0.98	0.07
	Max.	58.37	8.98	1.25	0.09
3	Mean	55.76	7.78	1.04	0.08
	SD	1.54	0.41	0.11	0.02
	Variance	2.36	0.17	0.01	0.00
	Min.	52.15	7.12	0.79	0.05
	Max.	58.26	8.98	1.25	0.12
4	Mean	54.38	7.49	1.00	0.07
	SD	1.62	0.27	0.16	0.02
	Variance	2.62	0.07	0.03	0.00
	Min.	51.05	6.98	0.69	0.05
	Max.	58.36	8.10	1.38	0.11
Polarity		+	+	−	−

Polarity: '+' = the higher the better criteria and '−' = the lower the better criteria.

to affecting the emission of CO_2, carbon has a role in the heating value of raw materials.

The results of proximate analysis (moisture and ash content, fixed carbon and volatile matter content) and HHV, LHV of oil cake are presented in Table 5, and the ANOVA calculation of these parameters in Table 7. Statistically significant differences of samples have been found in most cases, for various observed assays.

All of the samples had ash percent below 2.0, which is lower than literature data for olive cake pellets where 5.6% of ash was determined [16] and also lower than some other biomass pellets such as straw and grape pomace pellets [29,30]. When fuel with higher ash content is combusted, it causes the appearance of slag and deposit in the furnace and raises dust emissions [30]. As forest residues and wood contain less ash than agricultural biomass addition of those materials or combined pelletization can be used to lower the ash content [7,29].

Considering heating values of the pellets, they can be classified as a good fuel, since the values were high; HHV was above 22.0 MJ/kg, which is higher than wood pellets, which are mostly used as a fuel. Heating value of the biomass depends on its chemical and proximate composition. A higher proportion of carbon and hydrogen positively contributes to the heating value, as well as lower ash content [31].

Fixed carbon content varied between 14.27 and 17.97% which includes all the 36 samples. Biomass mainly contains lesser amounts of this parameter compared to solid fossil fuels, which is one of the reasons for its slightly lower heating value. A higher proportion of fixed carbon has an impact on increasing the calorific value of the fuel [32], so it's higher content is desirable characteristics for the fuel. Variation of its content comes primarily due to different chemical composition of biomass. For example, grape pomace has about 25% fixed carbon [29], while other agricultural residues like corn cob, wheat straw that is between 16 and 18% [33].

The highest average content of volatile matter had pellets from cultivar Leccino as shown in Table 5. Volatile matter is, like the content of fixed carbon, under the influence of moisture, ash, coke and the fixed carbon. For this reason, conditioning treatment had an effect on this parameter. Biomass contains more volatile compounds compared to fossil fuels. Higher level of volatiles contributes positively to heating value of the fuel [32].

As the statistical analyses showed conditioning temperature has been the most important variable for moisture content and fixed carbon. That is understandable since conditioning directly affects the moisture content of the material. Ash content and HHV are mostly affected by cultivar type, while LHV has been influenced almost equally by both conditioning temperature and binder percent. Fixed carbon and volatile content are complexly impacted by linear and nonlinear terms in ANOVA calculation.

Physical properties (particle density, abrasion and length) of different olive cultivars are presented in Table 6, and the ANOVA calculation in Table 7. Statistically significant differences have been found in most cases, mostly influenced by conditioning temperature ($p < 0.05$).

Particle density of all samples was above 1.20 g/cm^3, which is similar to density of wood pellets [35]. Density of pellets was dependent on parameters of conditioning treatment. Pellets conditioned at 50 °C had the highest density in comparison with pellets produced without steam conditioning or pellets made of material which was conditioned at 50 °C. Moisture of the material has an effect on the pellet density in a way that higher moisture content lowers the density of pellets [36]. For material conditioned at 80 °C this was consequence of lowered

Table 5
Proximate analysis of pellets.

Cultivar	Descriptive statistics	Moisture (%)	Ash (%)	HHV (MJ/kg)	LHV (MJ/kg)	Fixed carbon (%)	Volatile matter (%)
1	Mean	9.62	1.92	22.42	20.82	16.41	80.39
	SD	2.23	0.02	0.15	0.14	0.86	0.81
	Variance	4.99	0.00	0.02	0.02	0.74	0.66
	Min.	7.04	1.87	22.13	20.54	14.59	78.64
	Max.	12.50	1.97	22.75	21.11	18.26	81.95
2	Mean	9.62	1.92	22.42	20.82	16.41	80.39
	SD	2.10	0.02	0.22	0.24	0.75	0.87
	Variance	4.39	0.00	0.05	0.06	0.57	0.76
	Min.	6.10	1.51	22.10	20.33	15.42	77.90
	Max.	11.18	1.59	22.95	21.18	18.60	81.70
3	Mean	9.03	1.85	22.54	20.85	14.27	82.53
	SD	1.57	0.02	0.19	0.22	5.91	6.42
	Variance	2.48	0.00	0.04	0.05	34.89	41.26
	Min.	7.18	1.82	22.23	20.30	−1.86	78.79
	Max.	11.05	1.89	22.85	21.18	17.50	100.00
4	Mean	9.06	1.84	22.46	20.83	15.93	80.26
	SD	2.13	0.02	0.25	0.25	0.51	0.91
	Variance	4.56	0.00	0.06	0.06	0.26	0.83
	Min.	7.00	1.80	22.02	20.34	15.09	78.49
	Max.	12.00	1.89	22.96	21.33	17.21	81.60
Polarity		Opt. < 10%	−	+	+	+	+

Polarity: '+' = the higher the better criteria and '−' = the lower the better criteria.

Table 6
Physical properties of pellets.

Cultivar	Descriptive statistics	Particle density (g/cm^3)	Abrasion (%)	Length (mm)
1	Mean	1.24	9.51	11.94
	SD	0.02	3.93	1.14
	Variance	0.00	15.47	1.31
	Min.	1.20	5.18	8.78
	Max.	1.27	15.96	13.36
2	Mean	1.24	9.51	11.94
	SD	0.03	3.99	2.93
	Variance	0.00	15.91	8.57
	Min.	1.20	4.40	5.58
	Max.	1.31	15.21	13.38
3	Mean	1.26	7.06	11.03
	SD	0.03	2.84	2.38
	Variance	0.00	8.07	5.64
	Min.	1.21	4.00	6.70
	Max.	1.31	11.30	13.15
4	Mean	1.25	6.89	11.03
	SD	0.02	3.79	2.53
	Variance	0.00	14.35	6.40
	Min.	1.21	3.40	6.97
	Max.	1.30	13.90	13.49
Polarity		+	−	Opt. < 30 mm

Polarity: '+' = the higher the better criteria and '−' = the lower the better criteria.

Author's personal copy

Table 7
ANOVA table (sum of squares for each assay).

	Ultimate analysis				Physical properties			Proximate analysis					
	C	H	N	S	Particle density	Abrasion	Length	Moisture	Ash	HHV	LHV	Fixed carbon	Volatile
Interc.	334530*	6484*	98*	0.64*	170*	7161*	13494*	9015*	349*	54859*	47039*	26151*	703918*
C	98.97*	7.93*	2.31*	0.00*	0.01*	152.20*	23.76*	9.19*	2.09*	0.31*	0.01	134.25*	128.70*
T	3.99*	0.60*	0.01*	0.00*	0.03*	1242.54*	469.56*	406.45*	0.00*	0.06	0.10*	302.36*	99.47*
B	0.25	0.42*	0.01*	0.00*	0.02*	48.22*	1.37*	0.02**	0.00*	0.17*	0.08**	240.03*	101.36*
C × T	3.47*	0.64*	0.02*	0.00*	0.01*	46.24*	62.66*	19.11*	0.00*	0.16	0.21*	325.13*	240.50*
C × B	3.09*	0.77*	0.01*	0.00*	0.00*	8.49*	6.21*	0.01	0.01*	0.05	0.08**	199.62*	219.16*
T × B	0.82	0.01	0.01*	0.00*	0.00	20.79*	2.05*	0.01	0.00	0.05	0.04	5.00*	0.21
C × T × B	4.30*	0.25*	0.03*	0.00*	0.00*	31.68*	3.80*	0.07**	0.00*	0.39*	0.31*	23.12*	5.65*
Error	6.96	0.17	0.00	0.00	0.00	0.17	0.26	0.24	0.01	1.08	1.04	0.62	13.58

Error terms have been found statistically insignificant, C—cultivar, T—conditioning temperature, and B—binder.
Significant at:
* $p < 0.05$ level 95% confidence limit.
** $p < 0.10$ level 95% confidence limit.

friction in die channels, which caused lower compression force, and thus lesser compaction of material. On the other hand, water has binding effect due to formation of liquid bonds between particles. Therefore, lack of water in material which was not steam conditioned caused insufficient connection between particles, and thus pellets had lower density. It seems that conditioning temperature of 50 °C was optimal for production of dense pellets, which is important for the combustion characteristics for dense materials exhibit a longer burning time [30].

Abrasion was determined to establish the percentage weight loss of pellets "decay" in the dust due to mechanical damage during transport. This parameter has to be taken into account in the transport and combustion systems, as higher abrasion can cause malfunctioning of transportation systems, and also leads to higher dust emissions [30].

Abrasion values of the pellets varied from 3.43 to 15.29%, with significant differences within cultivars. The data obtained are consistent with the literature data where Miranda et al. [16] reported 8.59% abrasion (91.41% durability).

Conditioning of material and binder addition reduced abrasion of pellets of all cultivars. Conditioning increased the moisture content of the material as well as exposed it to higher temperatures, which facilitated the binding of particles [10]. Fasina [34] concluded that the increase in moisture from 5 to 10% reduced the abrasion of pellets from biomass, while a further increase in moisture content up to 20%, increased its value. Increasing the moisture content in material for pelletization can strengthen the bonds between the particles, but excess moisture can cause the opposite effect. Therefore, it is necessary to determine the optimum moisture content for specific raw material to be pelleted, depending on its chemical composition and/or physical properties. In this research pellets made of material conditioned at 80 °C (higher temperature and higher moisture content) resulted with the lowest abrasion of pellets. When comparing the results of abrasion of pellets for different binder content, it can be seen that all the pelleted samples had relatively high abrasion values. However, lowest average abrasion of pellets was achieved with addition of 2% of binder. Decrease in abrasion with addition of binder is in accordance with the literature data for wood pellets [35].

The length of pellets in this study ranged between 7 and 13 mm. Statistical analysis of the data presented in Table 7 showed a significant effect of cultivar and conditioning treatment on the length of pellets. Pellets made of unconditioned material were shorter for all cultivars, which indicate that increase of the moisture and temperature during conditioning process had an impact on the length of the pellet. This can be attributed to better bonding of the particles under the influence of conditioning, and thus decrease of number of weak points in the pellets. Water in the form of steam or liquid throughout formation of cohesive forces enables binding of particles in pellets. Additionally, water can promote chemical reactions between specific components, which can have beneficial effect on integrity of pellets [8,10]. Likewise with abrasion of pellets, binder content also showed a significant effect on the length of pellets. Optimal binder content for higher pellet length was 1%. Berghel et al. [37] also showed that addition of binder improved pellet length.

3.2. Standard score analysis

SS as the mean value of standard score transformed from the initial data generated with different methods (assays) for each item has been calculated assigning each applied measuring parameter equal weight. In this integrated approach SS is in a numerical scale with no units and has a consistent agreement with chemical and physical quality evaluation methods. Although it is a relative index and may not represent a specific property of different olive cake pellets characteristics, SS provides a reasonably accurate rank of olive cakes pellets.

In this article, standard scores are calculated for integrated chemical and physical characteristics and obtained data are presented in Table 8. SS above 0.60 stands for the high standard in chemical and physical properties. Olive cake pellets with SS value below 0.60 are attributed with poorer physical or chemical characteristics. Using the standard score analysis and revealing the SS of different olive cakes and different processing parameters can be referenced for developing strategies for improving final product characteristics. The addition of binder or additional thermal treatment could be introduced to reduce the negative effect of their inherent properties (cultivar type) on the final score.

Standard scores analysis showed that the optimum physical and chemical characteristics have been experienced with olive cultivar "Buža", conditioned at 50 °C, and with no binder added (0.66). Generally, cultivar Buža was the best cultivar, with the highest number of SS results (above 0.60, average was 0.62), followed by I. Bjelica (average was 0.58), while Leccino and Pendolino had the poorest pellet quality (averages were 0.55 and 0.53, respectively). As can be seen from SS analyses olive cake pellets with equally good characteristics can be produced by conditioning at 50 °C and without conditioning. Pellets produced from olive cake conditioned at 80 °C had lower quality. This is of great importance since conditioning rises the cost of pellet production.

Somewhat better quality pellets are obtained when adding binder to the material, but with no significant differences between 1 and 2%. Therefore addition of 1% could be recommended.

The addition of binder did not affect pellet quality as significantly as conditioning temperature (this was also concluded by ANOVA). This may be due to the low percent of binder, as previous investigation showed a considerable improvement in pellets physical characteristics when more binder (up to a certain point) was added [35,37]. However, this binder percentage range was chosen in the experiment while EU standards for fuel pellets allow additives up to 2%.

Author's personal copy

Table 8
Experimental design (coded) and SS of pellets.

Run no.	Cultivar	Temp. (°C)	Binder (%)	SS
1	1	1	1	0.60
2	1	1	2	0.58
3	1	1	3	0.65
4	1	2	1	0.62
5	1	2	2	0.62
6	1	2	3	0.59
7	1	3	1	0.51
8	1	3	2	0.50
9	1	3	3	0.53
10	2	1	1	0.63
11	2	1	2	0.60
12	2	1	3	0.63
13	2	2	1	0.66
14	2	2	2	0.63
15	2	2	3	0.63
16	2	3	1	0.57
17	2	3	2	0.59
18	2	3	3	0.61
19	3	1	1	0.53
20	3	1	2	0.65
21	3	1	3	0.64
22	3	2	1	0.45
23	3	2	2	0.54
24	3	2	3	0.54
25	3	3	1	0.48
26	3	3	2	0.54
27	3	3	3	0.42
28	4	1	1	0.59
29	4	1	2	0.62
30	4	1	3	0.63
31	4	2	1	0.58
32	4	2	2	0.57
33	4	2	3	0.60
34	4	3	1	0.48
35	4	3	2	0.47
36	4	3	3	0.40

3.3. Principal component analysis (PCA)

The PCA allows a considerable reduction in a number of variables and the detection of structure in the relationship between measuring parameters, different olive cultivars and process parameters that give complimentary information. All samples have been produced with different olive cultivars and various conditioning treatment and binder percent as shown by experimental design (Tables 3, 8) and predicted by PCA score plot (Fig. 1). The full auto scaled data matrix consisting of four different varieties of olive cultivars with different technological treatment are submitted to PCA.

For visualizing the data trends and the discriminating efficiency of the used descriptors a scatter plot of samples using the first two principal components (PCs) issued from PCA of the data matrix is obtained (Fig. 1). As can be seen, there is a neat separation of the four varieties of olive cake, according to used assays for all integrated chemical and physical quality. Quality results show that the first two principal components, accounting for 58.09% of the total variability can be considered sufficient for data representation and the first two principal components for integrated chemical and physical quality. Chemical parameters ash content, HHV and LHV have been found most influential for first factor coordinate calculation, while the contribution of moisture content, length and abrasion have been most important variables for factor coordinate calculation.

The influence of processing parameters can be observed on Fig. 1, with lower temperature regime at the bottom, and lower binder content at the right side of graphic. PCA graphic showed good discrimination characteristics between cultivars I. Bjelica and Buža, which were found different mostly due to their ultimate analysis properties, HHV, LHV and ash content. Leccino and Pendolino cultivars showed to be very influenced by binder content. Samples having the highest C and H, content (also HHV), located at the left side of PCA biplot graphic showed better SS results, 0.63–0.66, (No 13, 14 and 15). Samples with lower moisture content (No 10, 12, 19, 21 and 30) also showed better SS results, in range of 0.63–0.65. Low nitrogen and sulphur content have been observed for samples No 3, 4 and 5, which also showed better SS results.

4. Conclusion

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

Due to statistically significant differences among olive pellets samples (related to physical and chemical qualities), characterization of various olive cultivars, subjected to different technological treatments has been introduced.

The produced pellets had acceptable quality for energy utilisation. All the samples had high particle density, high heating values, low ash content and low sulphur content. The applied technological treatment had

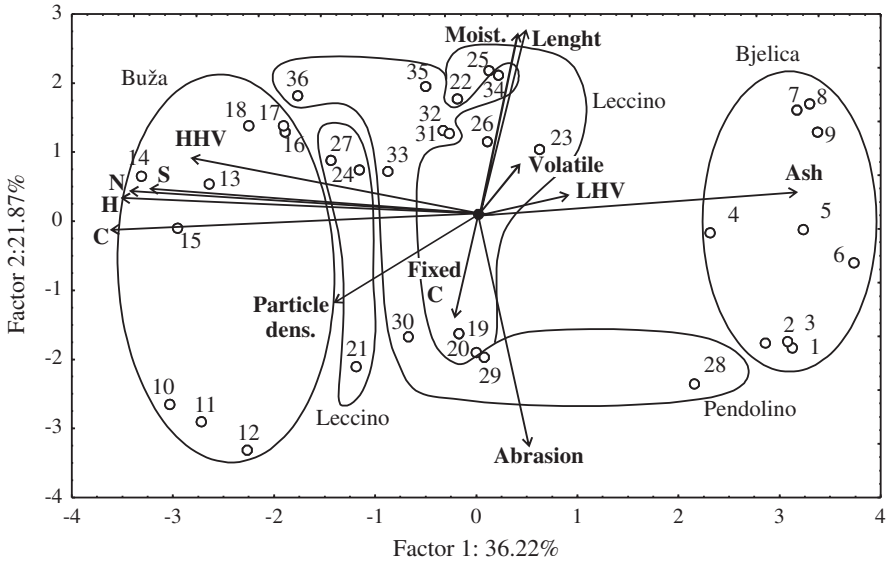


Fig. 1. Biplot for the characteristics of olive cake pellets.

Author's personal copy

statistically significant influence on fuel characteristics (fixed carbon and volatiles). Overall high contents of volatile substances and fixed carbon, were established which contributes to better combustion characteristics of pellets. The higher heating value was slightly influenced by the cultivar, with a heating value of all cultivars above 22 MJ/kg. From the above-mentioned it can be concluded that the pellets from olive cake present good fuel for heating energy generation.

Limitations regarding combustion of pellets can be established due to elevated nitrogen content and higher percent of abrasion. These defects can possibly be diminished by adding wood biomass to pelletization blend.

Since the pellet quality is influenced by so many parameters and they are altered as the technological treatments change, standard score analysis (SS) has been applied for evaluating the quality of pellets, in conjunction with PCA. These analyses compiled both physical and chemical properties uniting them into a unique system. Similar results have been obtained with both analyses, pointing out that olive pellets "Buža", processed at optimal processing parameters (temperature 50 °C, with no binder added), gained the best score (0.66 of 1.00). Generally cultivar "Buža" achieved the best pellet quality. It was concluded that equally good pellets can be produced with conditioning at 50 °C and without conditioning, while conditioning at 80 °C didn't achieve as good results. This is of great importance in practical pellet production, while it enables energy savings. In this manner the producers of olive oil could use their waste and successfully produce heating energy.

Using the principal component analysis (PCA) and revealing the coordinates of different olive cake pellet samples, the position regarding quality data and directions for the improving of their characteristics can be realized.

Acknowledgement

This article is written within the project III 46005, funded by the Serbian Ministry of Education, Science and Technological Development.

References

[1] G. Taralas, M.G. Kontominas, Pyrolysis of solid residues commencing from the olive oil food industry for potential hydrogen production, Journal of Analytical and Applied Pyrolysis 76 (2006) 109–116.
[2] Croatian bureau of statistics, Statistički ljetopis Republike Hrvatske, CROSTAT, RH, 2011.
[3] P.A. Fokaides, K. Tsiftes, Utilisation of Olive Husk in energy sector in Cyprus, Renewable Energy Sources & Energy Efficiency (2007) 28–30, (Nicosia, Cyprus).
[4] J. Werther, M. Saenger, E.U. Hartge, T. Ogada, Z. Siagi, Combustion of agricultural residues, Progress in Energy and Combustion Science 26 (2000) 1–27.
[5] M. Arshadi, R. Gref, P. Geladi, S.-A. Dahlqvist, T. Lestander, The influence of raw material characteristics on the industrial pelletizing process and pellet quality, Fuel Processing Technology 89 (2008) 1442–1447.
[6] R. Samuelsson, M. Thyrel, M. Sjöströmb, T.A. Lestander, Effect of biomaterial characteristics on pelletizing properties and biofuel pellet quality, Fuel Processing Technology 90 (2009) 1129–1134.
[7] C. Serrano, E. Monedero, M. Lapuerta, H. Portero, Effect of moisture content, particle size and pine addition on quality parameters of barley straw pellets, Fuel Processing Technology 92 (2011) 669–706.
[8] M. Thomas, D.J. van Zuilichem, A.F.B. van der Poel, Physical quality of pelleted animal feed. 2. Contribution of processes and its conditions, Animal Feed Science and Technology 64 (1997) 173–192.
[9] T. Brlek, M. Bodroža – Solarov, Đ. Vukmirović, R. Čolović, J. Vučković, J. Lević, Utilization of spelt wheat hull as a renewable energy source by pelleting, Bulgarian Journal of Agricultural Science 5 (18) (2012) 752–758.
[10] N. Kaliyan, R.V. Morey, Factors affecting strength and durability of densified biomass products, Biomass and Bioenergy 33 (2009) 337–359.
[11] W. Stelte, J.K. Holm, A.R. Sanadi, S. Barsberg, J. Ahrenfeldt, U.B. Henriksen, A study of bonding and failure mechanisms in fuel pellets from different biomass resources, Biomass and Bioenergy 35 (2011) 911–918.
[12] M. Masghouni, M. Hassairi, Energy applications of olive-oil industry by-products: — I. The exhaust foot cake, Biomass and Bioenergy 18 (2000) 257–262.
[13] H. Topal, A.T. Atimtay, A. Durmaz, Olive cake combustion in a circulating fluidized bed, Fuel 82 (2003) 1049–1056.
[14] M.T. Miranda, A. Cabanillas, S. Rojas, I. Montero, A. Ruiz, Combined combustion of various phases of olive wastes in a conventional combustor, Fuel 86 (2007) 367–372.
[15] T. Miranda, S. Román, J.I. Arranz, S. Rojas, J.F. González, I. Montero, Emissions from thermal degradation of pellets with different contents of olive waste and forest residues, Fuel Processing Technology 91 (2010) 1459–1463.
[16] T. Miranda, J.I. Arranz, I. Montero, S. Román, C.V. Rojas, S. Nogales, Characterization and combustion of olive pomace and forest residue pellets, Fuel Processing Technology 103 (2012) 91–96.
[17] T. Brlek, N. Voća, T. Krička, J. Lević, Đ. Vukmirović, R. Čolović, Quality of pelleted olive cake for energy generation, Agriculturae Conspectus Scintificus 1 (77) (2012) 31–35.
[18] NREL/TP-510-42622, Determination of ash in biomass, 2005.
[19] NREL/TP-510-42621, Determination of total solids in biomass and total dissolved solids in liquid process samples, 2008.
[20] CEN/TS 15148, Solid Biofuels—Method for the Determination of the Content of Volatile Matter, European Committee for Standardization, 2005.
[21] CEN/TS 15104, Solid Biofuels—Determination of Total Content of Carbon, Hydrogen and Nitrogen—Instrumental Methods, European Committee for Standardization, 2005.
[22] CEN/TS 15289, Solid Biofuels—Determination of Total Content of Sulphur and Chlorine, European Committee for Standardization, 2006.
[23] CEN/TS 14918, Solid Biofuels—Method for the Determination of Calorific Value, European Committee for Standardization, 2005.
[24] F. Rabier, M. Temmerman, T. Böhm, H. Hartmann, P.D. Jensen, J. Rathbauer, J. Carrasco, M. Fernández, Particle density determination of pellets and briquettes, Biomass and Bioenergy 30 (2006) 954–963.
[25] Statistica (Data Analysis Software System), v. 8.0, StatSoft, Inc., Tulsa, OK, USA, 2008, (http://www.statsoft.com).
[26] S.C. Sharma, Applied Multivariate Techniques, JohnWiley & Sons Inc., New York, 1996.
[27] J.H. Zar, Biostatistical Analysis, 3rd ed. Prentice Hall Inc., Upper Saddle River, N.J., 1996.
[28] V.K. Verma, S. Bram, F. Delattin, P. Laha, I. Vandendael, A. Hubin, J. De Ruyck, Agro-pellets for domestic heating boilers: standard laboratory and real life performance, Applied Energy 90 (2012) 17–23.
[29] M.T. Miranda, J.I. Arranz, S. Román, S. Rojas, I. Montero, M. López, J.A. Cruz, Characterization of grape pomace and pyrenean oak pellets, Fuel Processing Technology 92 (2011) 278–283.
[30] I. Obernberger, G. Thek, Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour, Biomass and Bioenergy 27 (2004) 653–669.
[31] A.A. Khan, W. de Jong, P.J. Jansens, H. Spliethoff, Biomass combustion in fluidized bed boilers: potential problems and remedies, Fuel Processing Technology 90 (2009) 21–50.
[32] R. Saidur, E.A. Abdelaziz, A. Demirbas, M.S. Hossain, S. Mekhilef, A review on biomass as a fuel for boilers, Renewable and Sustainable Energy Reviews 15 (2011) 2262–2289.
[33] PHYLLIS—A Database for Biomass and Waste, http://www.ecn.nl/phyllis Netherlands Energy Research Foundation ECN, Petten, Netherlands, June 2013 (Status).
[34] O.O. Fasina, Physical properties of peanut hull pellets, Bioresource Technology 99 (2008) 1259–1266.
[35] I. Mediavilla, L.S. Esteban, M.J. Fernández, Optimisation of pelletisation conditions for poplar energy crop, Fuel Processing Technology 104 (2012) 7–15.
[36] S. Mani, L.G. Tabil, S. Sokhansanj, Effects of compressive force, particle size and moisture content on mechanical properties of biomass pellets from grasses, Biomass and Bioenergy 30 (2006) 648–654.
[37] J. Berghel, S. Frodeson, K. Granström, R. Granström, M. Ståhl, D. Nordgren, P. Tomani, The effects of kraft lignin additives on wood fuel pellet quality, energy use and shelf life, Fuel Processing Technology 112 (2012) 64–69.