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## Changes in nutritional and energy properties of soybean seed and hull after roasting

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### Abstract

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After harvesting, soybean seed must be thermally treated because of the increased moisture content. The most common thermal treatment of soybean is roasting, with three indicators that are critical for the process itself: seed moisture content, roasting period and process temperature. Following the above-mentioned, the aim of this paper was to determine nutritional and energy changes in three soybean varieties ('Gordana', 'Sivka' and 'Slavonka'). After collecting the samples, the nutrient structure of the core and energy components of seed hull for each variety were determined before and after the heat treatment by roasting. The roasted soybean seeds of the specified varieties were dried by exposure to temperatures of 125°C and 135°C in the duration of 10, 20 and 30 minutes. The results show that significant changes occurred in nutritional properties of soybean seed core in relation to temperature and time of roasting, as well as to assortment. There are also significant differences in elements, which affects the energy properties of soy seed hulls depending on temperature and duration of the procedure.

**Keywords:** thermal treatment; nutritional values; energy values

Soybean (*Glycine max* (L.) Merr.) is an old arable crop and one of the first domesticated plants in history. In terms of oil production, soybean by far exceeds other oilseed crops and amounts to 35% of total world oil production. Soybean crop has numerous uses and when processed, it can be fully utilized (OVEIDO et al. 2011). Today, soybean seeds are used for producing oil and as a protein component in the human diet and animal nutrition (SOBCZAKA 2015). Soybean is the most popular and one of the most investigated leguminous crops, it is used in form of cooked seeds, flour, tofu, milk etc.; however, it is mostly grown as an oil plant for cooking oil production as well as oil for other uses. In the last decade, its residues (biomass) have been used as fuel (YOO et al. 2012).

The soybean fruit is a pod containing 2 to 5 seeds. Raw soybean seeds are not a desirable ingredient in animal nutrition because of their low digestibility,

which results in poor animal growth and is a potential cause of maldigestion. Nutritional properties of soybean core derive from its chemical composition and in average are made of 35–50% of protein, 18–24% oil, 34% carbohydrates, 5% ash and 10–13% moisture (VRATARIĆ et al. 2008). However, the main cause of low digestibility of raw soybean is a trypsin inhibitor. Moreover, raw soybean seeds contain urease enzyme, which, when in contact with urea (a component of animal feed for ruminants), compromises its efficiency in animal feeding.

After harvesting, soybean seed must be thermally treated because of an increased moisture content. Thermal treatment is any procedure where soybean seeds are exposed to increased temperature for a specific period of time. It includes drying, internal heating (infra-red and microwave radiation), pressing (extrusion, expansion, roller pressing) and roasting, all in order to increase digestibility of soy-

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beans. The result is higher digestibility of proteins since the process improves digestibility of amino acids and neutralizes anti-nutritional components (REDDY, PIERSON 1994; ADEYEMO, ONILUDE 2013).

The most common thermal treatment of soybean is roasting. The roasting technology is a thermal process that requires intensive heating; it is obtained by infra-red beams, but more often the process uses liquid or gaseous fuels and electric energy. The procedure includes roasting of beans at temperatures from 120°C–140°C up to 160°C, in order to enhance nutritional and physico-chemical characteristics of raw soybean (JURKOVIĆ et al., 1991). Three indicators are critical for the roasting procedure: seed moisture content, roasting period and process temperature (KATIĆ et al. 2004; KRIČKA 2004; MATIN et al. 2013). After roasting, the seeds have a brown colour and pleasant aroma. The roasting treatment eliminates the bitter taste that is characteristic for legumes including soybean seeds, and, most importantly, this process inactivates and thus eliminates the trypsin inhibitor activity in seeds.

Furthermore, after harvesting and treatment, the by-product of seed production is seed hull or crust. High energy costs, increased import of energy products, depleting of oil reserves and growing awareness about negative effects of consumption of oil resulted in growing needs of finding renewable energy sources. On a global scale, the most important renewable energy source is biomass obtained from the residues and remains from agricultural and forestry activity, because it consists of all biodegradable matters of vegetable and animal origin (GRAY et al. 2006). Such agricultural residue is soybean hull, which is made of hemicellulose (approx. 50%), cellulose and other non-cellulosic polysaccharides (MODIĆ 2004). Biomass is a very acceptable fuel in terms of environmental impact, because it contains traces - if any - of toxic substances, such as sulphur, heavy metals, etc., which are normally found in fossil fuels. The quality of biomass is determined by its carbon, hydrogen and nitrogen content, and moisture and ash levels, which all determine the energy potential of this material (VASSILEV et al. 2010).

Following the above-mentioned, the aim of this paper was to determine the nutritional and energy changes of three investigated soybean varieties ('Gordana', 'Sivka' and 'Slavonka') during a thermal treatment at temperatures of 125°C and 135°C for 10, 20 and 30 min, in order to achieve the efficient

use of energy, without affecting the quality of soybean seed during the process.

## MATERIAL AND METHODS

**Material.** Analyses of nutritional properties and elements that affect energy properties in soybean seeds were conducted on three varieties, 'Gordana', 'Sivka' and 'Slavonka', which are the most common soybean varieties used in Croatia. These were grown at the experimental field of the Faculty of Agriculture, Zagreb. 'Gordana' is a late variety of ripening group II, and the length of full vegetation is 140–145 days. 'Sivka' is an early variety of ripening group 0 with 115–125 days vegetation. 'Slavonka' is a medium early variety of ripening group I and its vegetation lasts 130–135 days.

**Treatment.** Roasting was conducted on a laboratory roaster („Seting inžinjering“, Delnice, Croatia), which consists of a drum with door and houses, and an 800 × 800 mm perforated plate. Hot air from the roaster is extracted by an axial fan. The roaster has three built-in PT 1000 probes for measuring air temperature at roaster's inlet and outlet points, and the temperature of soybean in the air current. The initial air-temperature regulation is manual and is switched to automatic afterwards. The air current rate after passing through the layer of samples was measured by use of a digital anemometer (Testo, Model 400, UK).

**Analytical methods.** Nutritional properties of the soybean core and elements that affect energy properties of the hull were tested before and after the thermal treatment consisting of conductive drying via roasting. As for nutritional characteristics of the core, water, ash, starch, raw fat and proteins were determined. As for elements that affect the energy properties, water, ash, coke, heating value, total carbon, hydrogen, nitrogen, sulphur and oxygen in the core and hull were observed.

The water content was determined according to the protocol (CEN/TS 14774-2:2009), ash content according to (CEN/TS 14775:2004), carbon, hydrogen, nitrogen and oxygen according to (HRN EN 15104:2011), sulphur according to (HRN EN 15289:2011), starch according to (HRN ISO 6493:2001), fats according to (HRN ISO 6492:2001), protein according to (HRN ISO 1871:1999). Also, upper and lower heating values were determined according to the method (HRN EN 14918:2010),

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Table 1. Nutritional properties of soybean seed

Variety	Moisture (%)	Ash (%)	Starch (%)	Fats (%)	Protein (%)
Gordana	13.93 ± 0.79 <sup>a</sup>	6.10 ± 0.01 <sup>a</sup>	1.35 ± 0.01 <sup>a</sup>	19.61 ± 0.01 <sup>a</sup>	42.72 ± 0.72 <sup>b</sup>
Sivka	14.85 ± 0.01 <sup>b</sup>	6.11 ± 0.01 <sup>a</sup>	1.68 ± 0.01 <sup>a</sup>	18.36 ± 0.02 <sup>b</sup>	43.20 ± 1.38 <sup>c</sup>
Slavonka	16.25 ± 0.12 <sup>c</sup>	6.15 ± 0.02 <sup>b</sup>	1.47 ± 0.01 <sup>a</sup>	23.17 ± 0.02 <sup>b</sup>	42.17 ± 0.30 <sup>b</sup>

mean values ± SD with the same letter are not significantly different ( $p < 0.05$ ) according to the Tukey's HSD test

Table 2. Elements that affect energy properties of soybean seed

Variety	Carbon (%)	Nitrogen (%)	Hydrogen (%)	Sulphur (%)
Gordana	64.13 ± 0.44 <sup>a</sup>	7.99 ± 0.11 <sup>c</sup>	5.75 ± 0.08 <sup>a</sup>	0.26 ± 0.01 <sup>a</sup>
Sivka	64.47 ± 0.46 <sup>a</sup>	7.81 ± 0.01 <sup>a</sup>	5.81 ± 0.03 <sup>c</sup>	0.22 ± 0.01 <sup>a</sup>
Slavonka	66.39 ± 0.19 <sup>c</sup>	8.23 ± 0.03 <sup>b</sup>	6.21 ± 0.09 <sup>b</sup>	0.24 ± 0.01 <sup>a</sup>

mean values ± SD with the same letter are not significantly different ( $p < 0.05$ ) according to the Tukey's HSD test

coke, combustible matters and volatile matters were determined according to the protocol (CEN/TS 15148:2005).

**Statistical analysis.** After collecting the data of laboratory research, a statistical analysis of the obtained data was carried out, in order to establish the differences due to the variety, temperature and roasting time for each variable. For this purpose, a statistical model was made which includes the ef-

fects of varieties, temperature and roasting time, as well as the effects of their interactions (cultivar × roasting temperature, variety × roasting time, roasting time × roasting temperature, variety × roasting temperature × roasting time).

Model of this three-factorial experiment (cultivar × roasting temperature × roasting time = 2 × 4 × 4) was analysed for each treatment using the statistical software package SAS version 9.1 (SAS Insti-

Table 3. Nutritional properties of roasted soybean seeds

	Moisture (%)	Ash (%)	Starch (%)	Fats (%)	Protein (%)
<b>Variety</b>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>
Gordana	6.33 ± 0.83 <sup>a</sup>	5.85 ± 0.22 <sup>b</sup>	1.76 ± 0.50 <sup>a</sup>	22.66 ± 1.96 <sup>a</sup>	44.68 ± 0.48 <sup>b</sup>
Sivka	6.18 ± 1.33 <sup>a</sup>	5.99 ± 0.57 <sup>a</sup>	1.56 ± 0.17 <sup>a</sup>	22.78 ± 2.43 <sup>a</sup>	44.44 ± 0.65 <sup>b</sup>
Slavonka	6.06 ± 0.93 <sup>a</sup>	5.85 ± 0.23 <sup>b</sup>	1.55 ± 1.55 <sup>a</sup>	22.74 ± 2.63 <sup>a</sup>	45.57 ± 0.83 <sup>a</sup>
<b>Temperature</b>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>
125°C	7.03 ± 0.77 <sup>a</sup>	6.07 ± 0.07 <sup>a</sup>	1.54 ± 0.18 <sup>a</sup>	20.95 ± 1.38 <sup>b</sup>	45.24 ± 0.88 <sup>a</sup>
135°C	5.35 ± 0.42 <sup>b</sup>	5.79 ± 0.22 <sup>b</sup>	1.71 ± 0.44 <sup>a</sup>	24.50 ± 1.58 <sup>a</sup>	44.55 ± 0.60 <sup>b</sup>
<b>Time</b>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>
10 min	6.75 ± 1.07 <sup>a</sup>	6.00 ± 0.07 <sup>a</sup>	1.72 ± 0.28 <sup>a</sup>	22.21 ± 2.77 <sup>b</sup>	44.78 ± 0.94 <sup>a</sup>
20 min	6.26 ± 0.98 <sup>a</sup>	5.92 ± 0.09 <sup>a</sup>	1.45 ± 0.12 <sup>b</sup>	22.01 ± 1.80 <sup>b</sup>	44.82 ± 0.68 <sup>a</sup>
30 min	5.56 ± 0.73 <sup>b</sup>	5.76 ± 0.27 <sup>b</sup>	1.70 ± 1.48 <sup>a</sup>	23.96 ± 1.83 <sup>a</sup>	45.08 ± 0.83 <sup>a</sup>
<b>Interaction</b>					
Varieties* Temperature	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>
Varieties*Time	0.0030 <sup>**</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>
Temperature *Time	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>
Varieties*					
Temperature*Time	0.0002 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>	< 0.001 <sup>***</sup>

mean values ± SD with the same letter are not significantly different ( $p < 0.05$ ) according to the Tukey's HSD test ; NS – not significant; \*\*\*, \*\*, \* – significant at  $p = 0.001$ ; 0.01; 0.05, respectively

tute, Cary, NC, USA) using the GLM procedures and the Tukey's test of multiple comparison with the level of significance  $p \geq 0.05$ .

## RESULTS AND DISCUSSION

The investigation of nutritional and energy characteristics of soybean seed started with analysing the raw samples as received. Tables 1 and 2 show the determined values; the data on moisture and ash content are given in Table 1 for a better reference, but are referred to further on, when the nutritional values and elements that affect the energy properties are discussed.

Investigation of nutritive properties of raw soybean seeds shows that there are significant differences in the moisture, ash, fats and protein content, while in the starch content such differences did not occur. Moisture content was somewhat above the literature references (ENSMINGER et al. 1990; QIN et al. 1996; SOROUR, UCHINO 2004). However, since the initial moisture depends on year and time of harvest, this was expected. Other values, regardless of variety, were consistent with the literature references (ENSMINGER et al. 1990; KRIČKA et al. 2003; KIŠ 2004; MILANKO et al. 2012). Elements that affect energy properties of raw soybean seeds indi-

cate that there are significant differences in carbon, nitrogen and hydrogen content, while there are no such large differences in the sulphur content.

After determining the properties of samples as received, soybean seeds were treated in a roaster at temperatures of 125°C and 135°C, for periods of 10, 20 and 30 minutes. Table 3 provides data regarding moisture, ash, starch, fats and proteins in roasted seeds, whereas Table 4 presents carbon, nitrogen, hydrogen and sulphur contents in roasted soybean seeds.

After roasting during different roasting periods and at different temperatures, the nutritional properties of the roasted core were also determined (moisture, ash, starch, fat and proteins). It was found that variety had no significant influence on moisture, starch and fat content. The temperature did not significantly affect the starch content, nor did the roasting period affect the protein content. After roasting, moisture and ash contents were significantly reduced, with significantly increased fat, starch and protein contents; this was in accordance with the literature references (WILSON et al. 1978; KIŠ 2004; ARI et al. 2012; KRIČKA et al. 2003; MILANKO et al. 2012).

In addition, after roasting treatment of different durations and at different temperatures, in observing the elements which affect on energy properties it was determined that variety did not have a sig-

Table 4. Elements that affect energy properties of roasted soybean seeds

	Carbon (%)	Nitrogen (%)	Hydrogen (%)	Sulphur (%)
<b>Variety</b>	< 0.001***	< 0.001***	< 0.001***	0.0245*
Gordana	57.38 ± 0.86 <sup>a</sup>	6.94 ± 6.94 <sup>a</sup>	5.12 ± 0.05 <sup>a</sup>	0.20 ± 0.01 <sup>a</sup>
Sivka	57.20 ± 1.09 <sup>a</sup>	6.95 ± 0.15 <sup>a</sup>	5.10 ± 0.08 <sup>a</sup>	0.20 ± 0.01 <sup>a</sup>
Slavonka	57.32 ± 1.11 <sup>a</sup>	6.91 ± 0.17 <sup>a</sup>	5.11 ± 0.07 <sup>a</sup>	0.20 ± 0.01 <sup>a</sup>
<b>Temperature</b>	< 0.001***	< 0.001***	< 0.001***	0.1076
125°C	58.13 ± 0.67 <sup>a</sup>	7.06 ± 0.05 <sup>a</sup>	5.16 ± 0.05 <sup>a</sup>	0.20 ± 0.01 <sup>a</sup>
135°C	56.47 ± 0.48 <sup>b</sup>	6.81 ± 0.09 <sup>b</sup>	5.06 ± 0.04 <sup>b</sup>	0.20 ± 0.01 <sup>a</sup>
<b>Time</b>	< 0.001***	< 0.001***	< 0.001***	< 0.001***
10 min	57.71 ± 1.37 <sup>a</sup>	6.95 ± 0.20 <sup>a</sup>	5.10 ± 0.06 <sup>b</sup>	0.21 ± 0.02 <sup>a</sup>
20 min	57.21 ± 0.75 <sup>ab</sup>	6.94 ± 0.09 <sup>a</sup>	5.15 ± 0.08 <sup>a</sup>	0.20 ± 0.01 <sup>b</sup>
30 min	56.97 ± 0.67 <sup>b</sup>	6.91 ± 0.13 <sup>a</sup>	5.07 ± 0.04 <sup>b</sup>	0.20 ± 0.01 <sup>b</sup>
<b>Interaction</b>				
Varieties × Temperature	< 0.001***	< 0.001***	< 0.001***	0.0017**
Varieties × Time	< 0.001***	< 0.001***	< 0.001***	0.7887 NS
Temperature × Time	< 0.001***	< 0.001***	< 0.001***	< 0.001***
Variety × Temperature × Time	< 0.001***	< 0.001***	< 0.001***	0.0001***

mean values ± SD with the same letter are not significantly different ( $p < 0.05$ ) according to the Tukey's HSD test; NS – not significant; \*\*\*, \*\*, \* – significant at  $p = 0.001$ ; 0.01; 0.05, respectively

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Table 5. Combustible properties and a higher (HHV) and lower heating value (LHV) of soybean hulls as received

Variety	Carbon (%)	Hydrogen (%)	Sulphur (%)	Oxygen (%)	Volatile matter (%)	Combustion matter (%)	HHV (MJ/kg)	LHV (MJ/kg)
Gordana	49.54 ± 0.16 <sup>a</sup>	4.72 ± 0.20 <sup>b</sup>	0.18 ± 0.01 <sup>a</sup>	52.73 ± 0.30 <sup>c</sup>	68.18 ± 0.70 <sup>a</sup>	76.32 ± 0.04 <sup>b</sup>	16.77 ± 0.03 <sup>b</sup>	15.71 ± 0.02 <sup>b</sup>
Sivka	48.41 ± 0.15 <sup>a</sup>	4.28 ± 0.06 <sup>c</sup>	0.11 ± 0.05 <sup>c</sup>	54.77 ± 0.29 <sup>a</sup>	66.91 ± 1.08 <sup>a</sup>	76.31 ± 0.03 <sup>c</sup>	17.12 ± 0.02 <sup>a</sup>	16.18 ± 0.02 <sup>a</sup>
Slavonka	49.33 ± 0.04 <sup>a</sup>	5.14 ± 0.07 <sup>a</sup>	0.14 ± 0.02 <sup>b</sup>	53.42 ± 0.39 <sup>b</sup>	66.24 ± 1.22 <sup>a</sup>	76.46 ± 0.02 <sup>a</sup>	16.46 ± 0.03 <sup>c</sup>	15.34 ± 0.03 <sup>c</sup>

mean values ± SD with the same letter are not significantly different ( $p < 0.05$ ) according to the Tukey's HSD test

Table 6. Non-combustible properties of soybean hulls as received

Variety	Moisture (%)	Ash (%)	Coke (%)	Fixed carbon (%)	Nitrogen (%)
Gordana	14.54 ± 0.27 <sup>b</sup>	5.81 ± 0.08 <sup>a</sup>	14.19 ± 0.94 <sup>a</sup>	8.15 ± 0.71 <sup>a</sup>	2.51 ± 0.02 <sup>a</sup>
Sivka	13.88 ± 0.01 <sup>c</sup>	4.74 ± 0.04 <sup>c</sup>	15.78 ± 1.31 <sup>a</sup>	9.41 ± 1.08 <sup>a</sup>	2.21 ± 0.02 <sup>b</sup>
Slavonka	15.84 ± 0.02 <sup>a</sup>	4.94 ± 0.05 <sup>b</sup>	16.62 ± 1.49 <sup>a</sup>	10.08 ± 1.22 <sup>a</sup>	2.11 ± 0.04 <sup>c</sup>

mean values ± SD with the same letter are not significantly different ( $p < 0.05$ ) according to the Tukey's HSD test

nificant influence on carbon, nitrogen, hydrogen and sulphur content; sulphur content is not affected by temperature levels, and nitrogen content does not depend on roasting time. After roasting, the carbon, nitrogen, hydrogen and sulphur levels were significantly lowered. It was noticed that carbon and nitrogen significantly fall, and hydrogen significantly and unevenly varies, while the sulphur

content does not vary in relation to temperature and time of roasting.

Since the hull was removed from the seeds, for the purpose of further investigation, the hull was defined as biomass and combustible and non-combustible properties were investigated in samples as received, as well as in the roasted samples of soybean hull. Table 5 shows combustible properties

Table 7. Combustible properties and a higher (HHV) and lower (LHV) heating value of roasted soybean hulls

Parameters	Carbon (%)	Hydrogen (%)	Sulphur (%)	Oxygen (%)	Volatile matter (%)	Combustion matter (%)	HHV (MJ/kg)	LHV (MJ/kg)
<b>Variety (V)</b>	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	0.0018**	< 0.001***
Gordana	45.72 ± 0.50 <sup>b</sup>	3.96 ± 0.16 <sup>a</sup>	0.10 ± 0.01 <sup>a</sup>	56.00 ± 0.55 <sup>b</sup>	65.23 ± 2.40 <sup>b</sup>	76.61 ± 0.50 <sup>a</sup>	16.02 ± 0.77 <sup>a</sup>	15.16 ± 0.63 <sup>ab</sup>
Sivka	45.71 ± 0.44 <sup>b</sup>	3.91 ± 0.07 <sup>a</sup>	0.09 ± 0.01 <sup>a</sup>	56.29 ± 0.56 <sup>ab</sup>	67.01 ± 1.83 <sup>a</sup>	76.48 ± 0.21 <sup>a</sup>	16.36 ± 0.59 <sup>a</sup>	15.50 ± 0.57 <sup>a</sup>
Slavonka	46.25 ± 0.88 <sup>a</sup>	3.99 ± 0.23 <sup>a</sup>	0.10 ± 0.01 <sup>a</sup>	56.45 ± 0.70 <sup>a</sup>	65.54 ± 2.97 <sup>ab</sup>	76.59 ± 0.32 <sup>a</sup>	16.02 ± 0.50 <sup>a</sup>	14.98 ± 0.43 <sup>b</sup>
<b>Temper. (T)</b>	< 0.001***	< 0.001***	< 0.001***	< 0.001***	0.4116 NS	< 0.001***	< 0.001***	< 0.001***
125°C	46.36 ± 0.60 <sup>a</sup>	4.09 ± 0.12 <sup>a</sup>	0.10 ± 0.01 <sup>a</sup>	56.05 ± 0.78 <sup>b</sup>	65.84 ± 2.50 <sup>a</sup>	76.62 ± 0.28 <sup>a</sup>	16.53 ± 0.45 <sup>a</sup>	15.52 ± 0.55 <sup>a</sup>
135°C	45.42 ± 0.33 <sup>b</sup>	3.82 ± 0.06 <sup>b</sup>	0.09 ± 0.02 <sup>b</sup>	56.44 ± 0.32 <sup>a</sup>	66.01 ± 2.59 <sup>a</sup>	76.50 ± 0.42 <sup>a</sup>	15.74 ± 0.56 <sup>b</sup>	14.90 ± 0.44 <sup>b</sup>
<b>Time (t)</b>	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***
10 min	45.77 ± 0.22 <sup>a</sup>	4.01 ± 0.16 <sup>a</sup>	0.10 ± 0.05 <sup>b</sup>	56.72 ± 0.46 <sup>a</sup>	67.61 ± 2.13 <sup>a</sup>	76.64 ± 0.46 <sup>a</sup>	15.89 ± 0.81 <sup>b</sup>	15.01 ± 0.66 <sup>a</sup>
20 min	46.01 ± 0.64 <sup>a</sup>	3.97 ± 0.18 <sup>ab</sup>	0.11 ± 0.01 <sup>a</sup>	56.08 ± 0.57 <sup>b</sup>	65.28 ± 2.88 <sup>a</sup>	76.65 ± 0.30 <sup>a</sup>	16.43 ± 0.66 <sup>a</sup>	15.39 ± 0.72 <sup>a</sup>
30 min	45.90 ± 0.97 <sup>a</sup>	3.88 ± 0.13 <sup>b</sup>	0.09 ± 0.02 <sup>c</sup>	55.93 ± 0.56 <sup>b</sup>	64.89 ± 1.58 <sup>a</sup>	76.39 ± 0.26 <sup>b</sup>	16.08 ± 0.19 <sup>ab</sup>	15.23 ± 0.15 <sup>a</sup>
<b>Interaction</b>								
V × T	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	0.1277 NS	< 0.001***
Va × t	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	0.0215*	< 0.001***
T × t	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***
V × T × t	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***	0.0095**	< 0.001***

mean values ± SD with the same letter are not significantly different ( $p < 0.05$ ) according to the Tukey's HSD test; NS – not significant; \*\*\*, \*\*, \* - significant at  $p = 0.001$ ; 0.01; 0.05, respectively

Table 8. Non-combustible properties of roasted soybean hulls

Parameters	Moisture (%)	Ash (%)	Coke (%)	Fixed carbon (%)	Nitrogen (%)
<b>Variety (V)</b>	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***
Gordana	7.02 ± 0.40 <sup>b</sup>	4.85 ± 0.44 <sup>a</sup>	17.89 ± 3.02 <sup>a</sup>	11.09 ± 2.35 <sup>a</sup>	1.75 ± 0.21 <sup>a</sup>
Sivka	7.19 ± 0.73 <sup>b</sup>	4.54 ± 0.21 <sup>b</sup>	15.65 ± 2.31 <sup>b</sup>	9.31 ± 1.83 <sup>b</sup>	1.73 ± 1.19 <sup>a</sup>
Slavonka	7.92 ± 0.75 <sup>a</sup>	4.72 ± 0.10 <sup>ab</sup>	17.50 ± 3.75 <sup>ab</sup>	10.77 ± 2.97 <sup>ab</sup>	1.80 ± 0.26 <sup>a</sup>
<b>Temperature (T)</b>	< 0.001***	< 0.001***	0.4087 NS	0.3588 NS	< 0.001***
125°C	7.56 ± 0.35 <sup>a</sup>	4.87 ± 0.34 <sup>a</sup>	17.12 ± 3.14 <sup>a</sup>	10.48 ± 2.47 <sup>a</sup>	1.94 ± 0.15 <sup>a</sup>
135°C	7.33 ± 0.22 <sup>b</sup>	4.54 ± 0.17 <sup>b</sup>	16.90 ± 3.27 <sup>a</sup>	10.31 ± 2.59 <sup>a</sup>	1.59 ± 0.12 <sup>b</sup>
<b>Time (t)</b>	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***
10 min	7.28 ± 1.02 <sup>a</sup>	4.89 ± 0.41 <sup>a</sup>	14.89 ± 2.67 <sup>b</sup>	8.71 ± 2.13 <sup>b</sup>	1.79 ± 0.07 <sup>a</sup>
20 min	6.66 ± 0.67 <sup>b</sup>	4.68 ± 0.12 <sup>b</sup>	17.83 ± 3.63 <sup>a</sup>	11.04 ± 2.88 <sup>a</sup>	1.81 ± 0.33 <sup>a</sup>
30 minuta	6.41 ± 0.75 <sup>b</sup>	4.54 ± 0.22 <sup>b</sup>	18.31 ± 1.99 <sup>a</sup>	11.42 ± 1.20 <sup>a</sup>	1.68 ± 0.17 <sup>a</sup>
<b>Interaction</b>					
V × T	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***
V × t	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***
T × t	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***
V × T × t	< 0.001***	< 0.001***	< 0.001***	< 0.001***	< 0.001***

mean values ± SD with the same letter are not significantly different ( $p < 0.05$ ) according to the Tukey's HSD test; NS – not significant; \*\*\*, \*\*, \* – significant at  $p = 0.001$ ; 0.01; 0.05, respectively

(carbon, hydrogen, sulphur, oxygen, volatile matters, as well as upper and lower heating values) of soybean hull samples as received. In addition, Table 6 presents non-combustible properties (moisture, ash, coke, fixed carbon (Cfix) and nitrogen) in the natural soybean hull samples.

In the analysis of variance shown in Tables 3 and 4, a highly significant interaction ( $p < 0.001$  \*\*\*) of all the investigated factors (variety × temperature × time) can be seen on the moisture, ash, starch, fats, proteins content, and also carbon, nitrogen, hydrogen and sulphur content in the roasted soya beans.

When soybean core as biomass is cleaned, the residue is soybean seed hull. The combustible and non-combustible matters were determined before and after roasting. The investigated combustible properties included carbon, hydrogen, sulphur, oxygen, volatile matters and combustible matters, higher heating value (HHV) and lower heating value (LHV). It was found that moisture, ash and nitrogen levels were significantly different, while no such differences were found in the coke and fixed the carbon content.

Soybean hull samples as received were roasted with air temperatures of 125°C and 135°C for 10, 20 and 30 minutes. Table 7 shows combustible properties in the roasted soybean hull at the above-mentioned parameters, whereas Table 8 shows non-combustible properties of the roasted soybean hull.

After roasting during different process periods and at different temperatures, the combustible and non-combustible properties were determined in the roasted soybean hulls. As for combustible matters, it was determined that hydrogen, sulphur, combustible matters and HHV are not influenced by the variety. Equally, air temperature did not significantly affect volatile matters and combustible matters. Moreover, the time of roasting did not significantly influence carbon, volatile matters and LHV. After roasting, the levels of carbon, hydrogen, sulphur, volatile matters, HHV and LHV significantly diminished, whereas with oxygen and combustible matters significant increased. The obtained results show that there are no considerable discrepancies from the literature data (BANASZKIEWICZ 2000; KRIČKA 2008; KIŠ et al. 2013).

As for the non-combustible properties in soybean hulls, it was determined that air temperature did not significantly influence coke and fixed carbon content. Furthermore, there were no significant differences in the nitrogen content in relation to variety and roasting period, while moisture, ash and nitrogen content significantly varied depending on variety itself, roasting period and temperature. After roasting, moisture, ash and nitrogen levels were found to be significantly reduced, with a significant rise in coke and fixed contents.

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Analysis of variance in Tables 7 and 8 show a highly significant interaction ( $p < 0.001$  \*\*\*) of all the investigated factors (variety  $\times$  temperature  $\times$  time) on the content of carbon, hydrogen, sulfur, oxygen, combustible substances, volatile substances content and a lower heating value LHV and also on moisture, ash, coke, fixed carbon and nitrogen content, while the share of higher caloric value of the investigated factors had a significant interaction ( $p = 0.0095$ ).

## CONCLUSION

The investigations followed how roasting influences nutritional properties and elements in terms of conductive drying, which affects the energy properties of the soybean varieties 'Gordana', 'Sivka' and 'Slavonka', the following conclusions can be drawn:

By observing the changes of nutritional properties of soybean seed core exposed to a conductive drying process by roasting in relation to temperature and drying period, it was determined that moisture and ash significantly decrease, and fat and protein significantly increase. Starch content varies considerably and unevenly in relation to temperature and roasting period, and also in selected varieties which differ by their morphological characteristics. Hence, from the aspect of nutritional properties, the variety selection must be defined for the need of sowing the crop for later use. In addition, since temperature and roasting time affect the quality of seed i.e., its nutritional properties and energy end-use due to the length of treatment, it is necessary to obtain optimization of the roasting time and temperature. The reduction of carbon, hydrogen, nitrogen and sulphur improves the digestibility to animals, especially ruminants.

Based on the observed changes of elements that affect energy properties of soybean seed hull during the conductive drying by roasting and are related to temperature and time of roasting, it was determined that carbon, hydrogen, sulphur and volatile matters significantly decreased after heat treatment, and oxygen and combustible matters significantly increased. The upper (HHV) and lower heating values (LHV) change significantly and unevenly after roasting. Non-combustible matter, water, ash and nitrogen considerably fell, while coke and fixed carbon levels become significantly higher. Namely, the heat value of biomass as fuel depends on the

quantity of carbon and hydrogen, so the energy value of hull diminishes with roasting, although the carbon and hydrogen levels remain rather high. Also, the reduced quantity of sulphur contributes to lowering the environmental pollution when this fuel is used.

Finally, soybean hull roasting was found to be good in terms of its non-combustible mineral particles – ash, which is being reduced; this indicates the quality of such biomass and its potential usability as a fuel.

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