Spanish Journal of Agricultural Research
13(1), e02-007, 9 pages (2015)
eISSN: 2171-9292
http://dx.doi.org/10.5424/sjar/2015131-6492
Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA)

RESEARCH ARTICLE

OPEN ACCESS

Reuse of rapeseed by-products from biodiesel production

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Abstract

The objective of this paper is to investigate usability of rapeseed cake from biodiesel fuel production as an energy source. For this research, rapeseed was grown at the research site of the Faculty of Agriculture in Zagreb, Croatia. The investigated rapeseed cake, residue from cold pressing, was divided in two groups of samples. The first group was a mix of three varieties (Bristol, Express and Navajo), while the other group consisted of three hybrids (Artus, Baldur, Titan). The utilization of rapeseed cake for energy via two routes was evaluated; namely, utilization of rapeseed cake as (1) solid biofuel (pellets) with addition of 3% of glycerol, and (2) as substrate in anaerobic digestion (AD). In investigation of cake as solid fuel, proximate (moisture content, ash content, fixed carbon and volatile matter), ultimate (content of carbon, sulphur, hydrogen, oxygen and nitrogen) and physical and calometry analyses (abrasion, diameter, length, density, higher and lower heating value were carried out. As for its use in AD, production of biogas during 40 days was monitored with a view of assessing the use of digested residue as fertilizer in agricultural production. Both groups of digested residues were analysed (pH, electroconductivity, moisture content, ash content, content of nitrogen and carbon, C/N ratio, content of P_2O_5, K_2O, Ca, Mg, Na). The analysis indicated that the investigated raw material is usable as solid and gas biofuel, and digested residue as fertilizer in ecological agriculture. The two groups of samples analysed here did not show significant differences.
Additional keywords: rapeseed cake; *Brassica napus*; pressing; pelletizing; biogas production; proximate and ultimate analysis
Abbreviations used: AD (anaerobic digestion); D (diameter); EC (electroconductivity); EU (European Union); HHV (higher heating value); L (lenght); LHV (lower heating value)
Citation: Krička, T.; Matin, A.; Voća, N.; Jurišić, V.; Bilandžija, N. (2015). Reuse of rapeseed by-products from biodiesel production. Spanish Journal of Agricultural Research, Volume 13, Issue 1, e02-007, 9 pages. http://dx.doi.org/10.5424/sjar/2015131-6492.
Received: 03 Jul 2014. **Accepted**: 13 Feb 2015
http://dx.doi.org/10.5424/sjar/2015131-6492

Funding: The authors received no specific funding for this work
Competing interests: The authors have declared that no competing interests exist.
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Introduction

The development of biodiesel production during the past thirty years has been rapid, from so called "backyard production" to industrial-scale production, and this fuel reached a significant role in arable and livestock farming (Krička *et al*., 2007). All member states of the European Union (EU) and most of the transitional countries have introduced biodiesel production based on different scenarios pending on their needs, use of different raw materials, manufacturers and, finally, end users. Due to increased consumption and simple utilization of diesel fuels the EU choose biodiesel as a priority biofuel in its endeavours to meet the targets set out in its Directive 2003/30/EC to promote the use of biofuels in transport. The critical raw material for biodiesel production is oil rape with a share of over 80% in global biodiesel production. In the Republic of Croatia oil rape is mainly grown for production of edible oil and grits or cake as by-product, which is used as a component in animal feed (Krička *et al*., 2004; Voća *et al*., 2008).

Since Croatia is a full member of the EU it must meet specific quotas of renewable energy which include biodiesel. The estimate is that until 2025 the quantity of rapeseed cake will reach as much as 468,000 tons. It is assumed that an increasing biodiesel production in Croatia, based on Directive 2009/28/EC and Ordinance on quality of biofuels (Official Gazette 141/2005), will create a problem of disposal of rapeseed cake as a by-product from biofuel production. Namely, following the experience of the EU countries with large production of biodiesel, it is estimated that the livestock farming, which in the last 20 years was reduced by half in Croatia, will not be able to absorb the amounts of cake generated in this process. Due to this and in order to maintain positive cost efficiency of biodiesel production at the EU markets which are saturated with this by-product, it is necessary to find new ways of using rapeseed cake.

One of such ways is thermal treatment of rapeseed cake which, through combustion in boilers, transforms rapeseed cake in solid fuel, primarily for heat production. In this case, after appropriate treatment, cake comes out as a CO_2-neutral fuel, which in the combustion process meets all ecological requirements and norms (Petersson *et al*., 2007).

As the EU has prescribed the obligation of technological disposal of agricultural waste, the most often applied technology of thermal treatment is pelletizing (Wolf *et al.,* 2006). Pelletizing is a thermo-plastic process of shaping material by extrusion, in which particles of raw material are shaped into compact pellets. In terms of energy production the most important factor of biomass pelletizing is the obtaining a product of better quality, higher density and higher volumetric heat value. All these properties enable lower transport and storage costs (Holtz, 2006). Pellets produced by this process are of regular shape, with a ≤25 mm diameter (D) and ≤5*D mm length (L) (Mani *et al.,* 2006; CEN/TS 14961:2005). In addition to its density, another important characteristic of good quality pellets is their wear resistance, *i.e.,* strength. The physical-chemical properties of pelletized biomass greatly influence the pelletizing process and quality of pellets, which is particularly evident in other sectors of the agricultural production, which is by itself exceptionally heterogeneous. If pelletizing conditions are properly defined, combustion process does not generate dust, generally a cause of a number of technical problems during furnace charging and combustion of the material (Holt *et al.*, 2006). When agricultural biomass and pellets are concerned, there are several standards that define their quality, the most important being the standard for liquid biofuels (CEN/TS). Introduction of these norms provided the basis for specific and cost efficient use of pellets.

Beside thermal treatment, anaerobic digestion (AD) is another method for effective use of rapeseed cake. During the last twenty years AD became an attractive method of processing high organic biomass, because its product is methane as s form of renewable energy (Chae *et al.,* 2008). Various designs of biogas plants provide possibilities of using different types of biomass as raw materials, from manure and slurry to slaughterhouse waste from food processing industry as well as different organic substrates. Organic biomass, including rapeseed cake, can be added in digesters during biogas production, and substrate composition largely determines the production and quality of biogas (Krička *et al.,* 2009). Digested residue, a by-product of AD and biogas production, can be used as organic fertilizer for crops and lawns and for irrigation of agricultural surfaces (Bilandžija *et al.,* 2009). Digested residue has several advantages when used as organic fertilizer, such as high nutritive content, humus properties and short maturation period (Dalemo *et al.,* 1998).

Given all these facts and taking into account that after using the quantities of rapeseed cake for animal nutrition, the issue to be addressed is the appropriate disposal of the excessive amounts of cake and their further use. Namely, investigated was the use of rapeseed cake as (1) solid biofuel (pellets) for direct combustion, with addition of 3% of glycerol (for heat production purposes), and (2) as substrate in AD (for electrical energy and heat production purposes). The objective of this work was to investigate the possible uses of rapeseed cake from biodiesel production.

Material and methods

Material

The investigations were carried out on cakes of six “00” genotypes of oilseed rape *(Brassica napus* L.): three line varieties (Bristol, Express and Navajo) and three hybrid varieties (Artus, Baldur, Titan) which were grown at the site of the Faculty of Agriculture in Zagreb during 2011. The samples were first coalesced and then separated in the separator in two procedures, each of them comprising of eight sub-separations, in accordance to the Rulebook on methods of sampling and quality control 137/2004 (Official Gazette, 2004).

Methods

Rapeseed was cold pressed in a disc pressing machine (Electrolux T20, Sweden), after extraction of oil from the seed, the raw material was divided in two groups. The first group of cakes consisted of varieties Bristol, Express and Navajo, while the second group consisted of cakes of three hybrids: Artus, Baldur and Titan. After pressing, all variety/hybrid cakes were mixed in equal proportions within a sample. The investigation process started by grinding in a laboratory grinder “IKA MF 10” with an average screen diameter of <0.5 mm. The samples were then pelletized in a laboratory pelletizer (Pellet Press 14-175; Kahl, Germany), after which the analyses of their energy usability were conducted.

Proximate analysis. The characteristics of the samples were determined by proximate analysis according to standard methods: moisture content (CEN/TS 14774-2:2004) in a laboratory oven (INKO ST-40, Croatia); while ash content (CEN/TS 14775:2004), fixed carbon (by difference), and volatile matter (CEN/TS 15148:2005) were determined by using a muffle furnace (Nabertherm GmbH, Nabertherm Controller B170, Germany).

Ultimate analysis. Total carbon, hydrogen, nitrogen and sulphur were determined simultaneously, by method of dry combustion in Vario Macro CHNS analyzer (Elementar Analysensysteme GmbH, Germany), according to the protocols for determination of carbon, hydrogen and nitrogen (HRN EN 15104:2011) and sulphur (HRN EN 15289:2011). Oxygen content was calculated by difference.

Calorimetry. Heating value was determined by the ISO method HRN EN 14918:2010 using an IKA C200 oxygen bomb calorimeter (IKA Analysentechnik GmbH, Heitersheim, Germany). A quantity of 0.5 g of each sample was weighted in a quartz crucible and put in a calorimeter for combustion. Higher heating value was obtained after combustion, by using the IKA C200 software. Heating value is reported in MJ/kg on dry basis.

Biogas production

The analysis of biogas production was carried out in the laboratory biogas plant of the Faculty of Agriculture in Zagreb. The lab plant consists of a water bath, mixer and a stainless steel batch fed reactor, and provides full simulation of the conditions of a large scale industrial plant for biogas production (Fig. 1). The investigation was focused on the possibility of using rapeseed cake as a raw material for biogas production by adding inoculum. The inoculum used for this purpose was the digested residue from the biogas plant Osatina Ivankovo, Croatia. Anaerobic digestion was conducted in mesophilic conditions at temperature of 35°C during a 40-day period. During digestion process, biogas production was measured daily, and biogas composition was analysed in a gas chromatograph CP-3800 (Varian, USA), in accordance with the method HRN EN 6974-4:2008. The biogas production investigation was conducted in triplicate.

Residue from AD and biogas production presents a very suitable material that can be used as bio-fertilizer. Therefore, this investigation also encompassed the analysis of the material content in order to establish whether it meets the requirements set out in the Croatian Regulation on ecological agricultural production (Official Gazette 10/2011). The pH value was determined directly from the samples in a pH-meter with combined electrode; electroconductibility (EC) was determined by use of a conductometer MA5964 with combined electrode, and total nitrogen was determined by the Kjeldahl

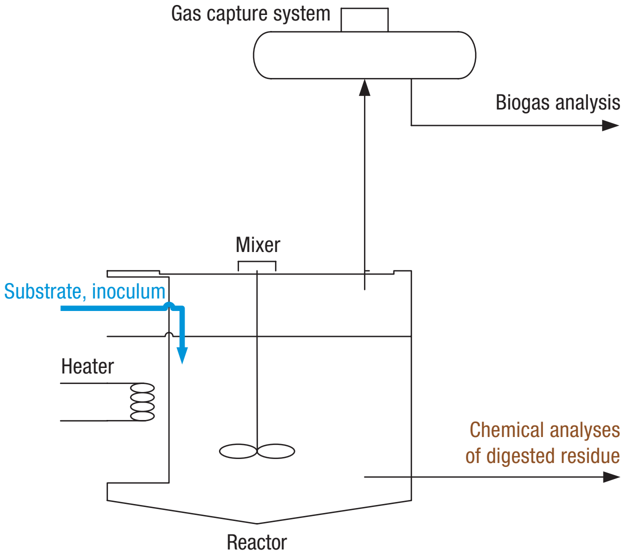

Figure 1. Design of laboratory biogas plant used for biogas for production.

method. Phosphorus was determined by molybdate-blue method on a UV/VIS spectrophotometer PU 8600, K and Na were determined by flame photometry and all other elements (Ca, Mg, Mn, Zn, Cu, Fe, Pb, Cd, Ni, As, Hg, Co, Cr) by atomic absorption spectroscopy (APHA, 1995). The samples were burned in a microwave oven Ethos D (Milestone, England), in accordance the supplier application notes for microwave digestion.

Statistical analysis

Since the design of the experiment was not specifically defined (the allocation was made on an absolutely random basis with various numbers of observations), the average values for each investigated factor were calculated and interaction was included in the relevant analysis. All measurements were carried out in triplicates. All data were analysed according to the generalized linear model (GLM) procedure in the statistical analysis system package version 8.00 (SAS, 1997). Data were expressed as means and, if justified by the statistical probability ($p<0.05$), subjected to the Duncan's new multiple range test. Differences were considered as statistically significant if $p<0.05$.

Results and discussion

Rapeseed cake as solid biofuel

The proximate, ultimate and physical analyses of the investigated groups of rapeseed cake after pelletizing are presented in Tables 1, 2 and 3. The samples were compared against CEN/TS 14961:2005 as the referent standard for solid biofuels quality.

Table 1 shows that moisture content was approximately (7.00-7.31%) in both samples, which is similar to that of olive cake, as described in the available literature (Al-Widyan *et al.,* 2006; Mirande *et al.,* 2007; Chouchene *et al.,* 2012). Moreover, ash content was somewhat above 7.0% which is a value higher than expected, but it remains within the upper limit of the CEN/TS 14961:2005 standard; high content of ash could be an effect of soil fertilization during rapeseed cultivation. The found fixed carbon values were between 16.52% and 16.84%, while volatile matter was around 69%. Similar results were obtained in the investigations conducted on olive cake by Al-Widyan *et al.* (2006), Mirande *et al.* (2007) and Chouchene *et al.* (2012), where fixed carbon was between 9.94 and 23.4%, while volatile matter was between 67.7 and 80.19%. High volatile matter content indicates that during combustion most of the biomass material will volatilize and burn as gas within the system. On the other hand, high fixed carbon content is a characteristic of herbaceous agricultural biomass residues (Vassilev *et al.,* 2010); it produces char and burns as a solid material in the combustion system (Kreil & Broekema, 2010). Thus, such high levels have positive effect on combustion properties.

The ultimate analysis results show values of C, S, H, O and N content respectively, which are in accordance with the CEN/TS 14961:2005 standard for solid biofuels. Namely, this standard does not set up specific values for rapeseed cake, but does give the ones for olive cake, as a by-product from food processing.

Table 1. Proximate analysis of investigated samples of rapeseed cake.

Sample	MC (%)	AC (% db*)	FC (% db)	VM (% db)
Rapeseed cake-hybrids	7.00	7.05	16.52	69.20
Rapeseed cake-varieties	7.31	7.11	16.84	68.98
Significance	NS	NS	NS	NS

%db = % on dry basis; MC = moisture content; AC = ash content; FC = fixed carbon; VM = volatile matter; NS = non-significant.

Of all elements, only H and N slightly exceed the standard values; this could be due to a more intensive soil fertilization of rapeseed comparing to olive cultivation.

The physical values prescribed in CEN/TS 14961:2005 for wooden pellets are the following: diameter (D) up to 25 mm, length (L) up to 5·D, abrasion (<2.3%) and density (>1.12 g/dm^3). Thus, it can be determined that both groups of the observed samples fully comply with the standards for these parameters. CEN/TS 14961:2005 is a norm which sets out energy standard for olive cake among other raw materials that are potential source for solid biofuels production, while standards for rapeseed cake have not been defined. The analysed samples were compared with olive cake because it is the most similar material to rapeseed cake in terms of utilization and production technology. The data of this Technical Specification were obtained from a combination of researches mainly from the Austrian, Dutch, Italian, Greek and Spanish sources. These values describe properties that can be expected in Europe in general.

Heat content, a very important factor which affects utilization of any material as a fuel, is influenced by the proportion of combustible organic components contained in it (Kataki & Konwer, 2001). It is related to the oxidation state of the natural fuels in which carbon atoms generally dominate and overshadow small variations of hydrogen content (Demirbas, 2004). Higher heating value (HHV), defined as a latent heat of the water vapour products of combustion, was found to be above 18.00 MJ/kg, which is in accordance with the applicable standard for solid biofuels, while lower heating value (LHV) was above 16.00 MJ/kg.

In all parameters presented in the Table 1 (proximate analysis), Table 2 (ultimate analysis) and Table 3 (physical and calorimetry analysis) no significant differences were found.

Rapeseed cake as substrate in anaerobic digestion

Biogas productivity was obtained for both types of the rapeseed cake samples, and the results are shown

Table 2. Ultimate analysis of investigated samples of rapeseed cake.

Sample	C (% db)	S (% db)	H (% db)	O (% db)	N (% db)
Rapeseed cake-hybrids	47.07	0.62	7.43	38.39	6.51
Rapeseed cake-varieties	46.57	0.63	7.34	38.77	6.72
Significance	NS	NS	NS	NS	NS

% db = % on dry basis; NS = non-significant.

Table 3. Physico-chemical and calorimetry analysis of investigated samples of rapeseed cake.

Sample	Abrasion (%)	Diameter (mm)	Length (mm)	Density (kg/dm^3)	HHV (MJ/kg)	LHV (MJ/kg)
Rapeseed cake-hybrids	2.20	6	13	1.18	18.32	16.99
Rapeseed cake-varieties	2.21	6	13	1.21	18.09	16.49
Significance	NS	NS	NS	NS	NS	NS

HHV = higher heating value; LHV = lower heating value; NS = non-significant.

in Fig. 2. The rise of productivity was exponential during the first twenty-odd days and the maximum value for these materials (variety cake/ hybrid cake) was reached around 22nd day of the process. Also, productivity was continuous for about 36 days from the start of the process, when a slight decline followed. Comparing the analysed production of biogas on a daily basis with the data obtained by Tekin & Dalgiç (2000) and Petersson *et al.* (2007) during AD of olive cake and rapeseed cake, the traceability of the data was observed. The mentioned authors obtained the highest production of biogas on the 20th day of the process. The production results published by Tekin & Dalgiç (2000) are fully consistent with the data quoted in this paper. This is different from Petersson *et al.* (2007) who obtained significantly lower production due to the acclimatization of microorganisms.

Table 4 shows medium values of physical-chemical analyses of digested residues (rapeseed cake of varieties and hybrids) after AD. In order to achieve optimal decomposition of the substrate in to methane and carbon dioxide, during digestion, the tendency should be towards neutral value of the digested material. One of the most important parameters for efficient and good quality production of methanogenic bacteria is the pH value. Liu *et al.* (2008) quote the optimal pH ratio for the most efficient gas production (6.5-7.5). Also, constant monitoring of pH value in digester is essential because its sudden drop may result in premature ceasing of biogas production. However, a reduced pH value (reaction) of the investigated raw materials may be caused by a higher concentration of lignocellulose material during AD, which was corroborated by Al-Masri (2001) in his investigations of digested residue from olive cake. In the investigated samples a mild alkaline reaction of digested residues was found (pH=5.27–5.30), which is most probably caused partly by increased Ca content. It can be concluded that the pH value is approximately within acceptable limits. Determination of electroconductivity (EC) in digested residues is aimed at establishing total quantity of salt in the solution because of soil salinization caused by fertilizers (Voća *et al.,* 2005). The EC values of the hybrid cake/ variety cake were within a range of 2.22 to 2.24 mS/cm. Al-Masri (2001) determined EC of olive pomace at 2.19-2.26 mS/cm and emphasized that EC declines in relation to percentage of lignocellulose substance in the digester as is the case with pH value. It is essential to monitor the content of these key biogenic elements in the substrates, *i.e.,* content of Ca, Mg and Na. The results for Ca content in the digested residues were within the limits of 0.42% for variety rapeseed cake and 0.44% for hybrid rapeseed

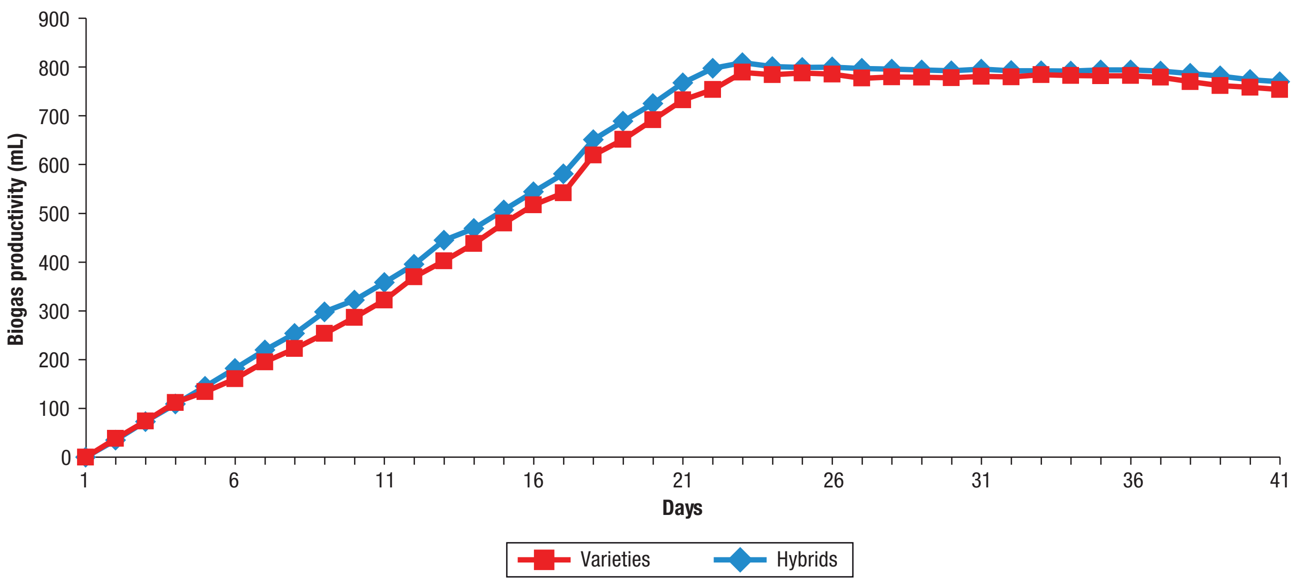

Figure 2. Biogas production rate during anaerobic digestion of the investigated rapeseed cake samples.

Table 4. Physico-chemical analysis of anaerobic digestion residues of investigated rapeseed cake samples.

Type of analysis	Rapeseed cake		*p* value
	Hybrids	Varieties	
pH	5.30	5.27	NS
EC (mS/cm)	2.22	2.24	NS
MC (% db)	80.40	80.07	NS
AC (% db)	6.92	6.88	NS
N–total (% db)	4.41	4.44	NS
C–total (% db)	38.60	38.57	NS
C/N ratio (% db)	8.74	8.78	NS
P_2O_5 total (% db)	0.53	0.50	NS
K_2O total (% db)	1.03	1.05	NS
Ca total (% db)	0.74	0.72	NS
Mg total (% db)	0.37	0.37	NS
Na total (% db)	0.05	0.04	NS

% db = % on dry basis; MC = moisture content; AC = ash content; NS = non-significant.

cake. Contents of Mg (0.37%) and Na (0.04-0.05%) were also determined in the digested residues, and these values were identical in both investigated types of cake. The comparison of the found Ca, Mg and Na values against literature data for olive cake (0.51-10.22%; 0.09-0.67%; 0.02-0.13% respectively) shows a slight variation of Ca percentage content, while Mg and Na are in line with the literature data (Environmental Impact Assessment, 2004). High moisture content usually facilitates AD, but it is difficult to maintain the same availability of water throughout the digestion cycle (Hernandez-Berriel *et al.,* 2008). Also, the chemical analysis of the digested residues showed equal moisture content. So, hybrid cake with 80.40% humidity content had only slightly higher percentage of moisture compared to 80.07% humidity content of variety cakes. It has been reported that the highest methane production rates occur at the humidity level of 60–80% (Bouallagui *et al.,* 2003). Therefore it can be concluded that the investigated substrates have moisture levels almost optimal for biogas production. The analysis of ash showed the content of organic and mineral matter in the samples; ash percentage content was found in a range from 6.88% in digested residue from variety cake to 6.92% in digested residue from hybrid cake, while ash content of 7%, found in olive pomace, is consistent with literature sources (Chouchene *et al.,* 2012).

In order to determine whether the samples of the investigated digested residues are suitable for fertilization of agricultural soil, the ratios were calculated of main biogenic elements -N, P and K. The result was 8.32:1:1.94 for hybrid cake and 8.88:1:2.10 for variety cake. For example, specific ratio of nutrients for cereal grains is 1.2:1:1.5; for potato 1:1:1.8; for grass 2.4:1:1 (Kaltwasser, 1980). It is evident that with such relations the digested residues can meet the plants' needs for all elements that were analysed and that there is an increased level of nitrogen, as in the case of pellets. In general, bio-fertilizers have a narrow C/N ratio, from 10:1 to 15:1 (Voća *et al.,* 2005). The same C/N ratio was found (8.7:1) in the investigated digested residues of rapeseed cake. Also, the ratio observed was somewhat lower than the one previously quoted.

Determination of heavy metals in the digested residues is important not only for environmental considerations but also because of the methanogenic bacteria in AD. For efficient growth of all methanogenic bacteria relatively high levels of iron, nickel and cobalt are required (Ram *et al.,* 2000). However, optimal concentrations of iron, nickel and cobalt were found in the digested residues in very wide variations (Gonzales-Gill *et al.,* 1993; Jarvis *et al.,* 1997; Mochinaga *et al.,* 1997; Takashima & Speece, 1997; Basiliko & Yavitt, 2001; Kida *et al.,* 2001). Such variations can be explained by presence of different varieties of methanogenic bacteria in the substrates and their different and particular needs for iron and cobalt. Due to this, low levels of some of these metals may result in limiting the whole process of biogas production. On the other hand, a higher metal concentration may cause toxicity, *i.e.,* it may prevent development of methane producing bacteria (Nies, 1999). In terms of environmental protection, damaging substance is any substance which is found in the agricultural soil in such concentrations which either temporarily or permanently compromise its fundamental role of being appropriate habitat for cultivated and feral vegetation. Allowed is the utilization of digested residues on arable surfaces, meadows and plain pasture grounds where soil contains some of heavy metals and persistent organic harmful matters in amounts below 50% of limit values set out in the regulation on ecological agricultural production in the Republic of Croatia (Official Gazette 91/2001). As it is evident from the data shown in Table 5, the concentrations of these heavy metals found in all samples of digested residues are below the prescribed limits and meet the requirements set out in the Republic of Croatia and, therefore, can be used without restrictions in ecological agricultural production.

Similarly to the parameters found in proximate analysis, ultimate analysis and physical and calorimetry analysis of rapeseed cake, chemical analysis (Table 4) and heavy metal analysis of the digested residue (Table 5) showed no significant differences.

With the production of the first generation biodiesel fuel in the Republic of Croatia as well as with the production needs in the future, Croatia is faced with the excess of rapeseed cake as its by-product. As an effect of the Homeland War the Croatian livestock has been reduced by 50% from the previous levels, which seriously limits the possibilities of the livestock farming to absorb total amounts of rapeseed cake. For these reasons, this work investigates the potential utilizations of rapeseed cake as an energy product, in form of solid fuel pellets as a raw material for production of biogas by alkaline digestion in biogas plants. Since this process leaves digested residue, this investigation aims to assess the quality of this by-product. In addition to variety rapeseed, there is an increasing use of hybrids in the Republic of Croatia, so the investigations included the cakes of rapeseed "00" cultivar varieties (Bristol, Express and Navajo) and three hybrids (Artus, Baldur, Titan) in order to identify eventual differences. Solid fuel from variety/hybrid rapeseed cakes was produced by pelletizing because of higher quality of the product *i.e.,* its better physical-chemical characteristics. The results showed no significant differences between the variety/hybrid cakes when the pellet production is concerned. Namely, physical-chemical analysis of the pellets discovered approximately equal parameters (radius, length, moisture, density and abrasion). However, it can be noted that there is a somewhat higher content of ash as well as an increased level of fixed carbon and volatile matter, which is most probably a characteristic of herbaceous agricultural biomass residues. The results of the ultimate analysis show contents of C, S, H, O and N, which are in accordance with the CEN/TS standard for solid biofuels. Namely, this standard does not set up specific values for rapeseed cake, but does give the ones for olive cake, as a by-product of food processing. Of all elements, only hydrogen and nitrogen contents slightly exceed the standard values. Higher heating value (HHV), defined as latent heat of water vapour products of combustion, was found at levels above 18.00 MJ/kg, which is in accordance with the applicable standard for solid biofuels, while lower heating value (LHV) was above 16.00 MJ/kg. It results that 1 kg of oil (41.00 MJ/kg) can be replaced with 2.56 kg of pellets obtained from the cakes of variety/hybrid rapeseed.

In addition to investigating pelletizing cake by thermal processing, the aim of this investigation was to determine the possibility of using variety/hybrid rapeseed cakes in biogas production as well as the quality of digested residue from biogas production. When the biogas production from variety rapeseed cakes is compared to that from cake of hybrid origin, there is no significant difference between the two materials. However, the analysis of biogas production shows that maximum production is obtain on around 20^{th} day of the process, which is relatively late. It is proposed that the rapeseed cake be used only as one of the components in a mix with other ingredients, rather than as a single component. After completion of the biogas production process it can be determined that there are no significant differences in the chemical composition of the digested residue between cakes of variety origin and those of hybrid origin. Additionally, the values of all the elements required under the Regulation on ecological agricultural production in the Republic are such that the obtained digested residue is assessed as suitable for use in the agricultural production as fuel.

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Table 5. Analysed values of heavy metals in investigated digested residues of two groups of samples (cake from hybrid oil rape and variety oil rape).

Chemical analysis mark (mg/kg)	Oil rape cake		Regulation on ecological agricultural production in Croatia	*p* value
	Hybrids	Varieties		
Mo	5.34	5.47	10	NS
Fe	310.62	309.87	–	NS
Zn	82.10	80.47	210	NS
Cu	9.34	8.40	70	NS
Pb	3.50	3.64	–	NS
Cd	0.50	0.47	0.7	NS
Ni	btl	btl	42	–
As	btl	btl	10	–
Hg	Traces (<0.1)	Traces (<0.1)	0.7	–
Co	0.21	0.25	50	NS
Cr	0.58	0.54	70	NS

NS = non-significant.

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