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Proximate, Ultimate, and Energy Values Analysis of Plum Biomass By-products Case Study: Croatia's Potential

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ABSTRACT

In many European countries, residues from agricultural products represent a considerable potential for development of bio-energy industry. A significant part of these biomass materials come from the fruit-growing business, i.e., primary fruit production and fruit processing plants. The EU directives require that the disposal of such residues should be environmentally sustainable. The objective of this study was to determine proximate (moisture content, ash, fixed carbon, volatile matter), ultimate (carbon, hydrogen, nitrogen and sulphur) and energy values (higher, lower) of biomass, as well as the Croatian total energy potential generated after the pruning (pruned residues) and processing of plum fruit (stone). Five different plum varieties (Bistrica, Cacanska ljepotica, Cacanska rodna, President, and Stanley), most commonly grown in the territory of Croatia, were analyzed and compared. The analyzed data were compared with the norm CEN/TS 14961 (2005) for solid biofuels and the data from the relevant literature. Both types of investigated biomass proved to be highly valuable sources of energy; and no significant difference between investigated plum varieties were found. Lower heating value, as one of the fundamental parameters of the biomass energy efficiency, averaged in the studied samples: 15.2 MJ kg^{-1} for plum pits and 17.12 MJ kg^{-1} for pruned biomass, which classifies plum biomass as a valuable energy raw material. Also, the calculations show that the potential production of the biomass available in Croatia could reach up to 292.13 MJ of renewable "green" energy annually.

Keywords: Agricultural residues, Biofuels, Pruned residues, Renewable green energy.

INTRODUCTION

Increasing energy demand and problems caused by intensive use of fossil fuels force the countries to use cleaner and more reliable energy sources. As a part of the search for alternative sources, many countries have taken actions to increase the share of renewable energy sources in electricity generation. (Sirin and Ege, 2012). In the European Union, there is a significant potential for agricultural companies and larger businesses to become independent producers of "green" energy through the combustion of biomass that derives from their own operations. It should also be emphasized that the term 'biomass' encompasses all biodegradable substances of vegetable and animal origin, generated from residues deriving from agriculture, forestry and similar industries (2003/30/EC). Following coal and petroleum, biomass is the third largest primary energy source on a global scale (Hashem *et al*., 2013). It is still the main source of energy for more than half of the world's population and provides about 1.25 billion tons of oil equivalent (toe) of primary energy, which makes about 14% of the world's annual energy consumption (Purohit *et al*., 2006; Zeng *et al*., 2010).

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In Europe, agricultural residues represent an important energy potential (around 250 million tons per year) for development of bio-energy industry in many countries. Meanwhile, a large portion of agricultural residues is made of residues from the fruit industry, i.e., from primary production and processing sector combined (pruned biomass of permanent plantations, stone-fruit pits, kernel-fruit crust). However, in some countries this material is still treated as waste, which is frequently disposed in an ecologically unsustainable way. (Di Blasi *et al*., 1996; Kricka *et al*., 2012). Moreover, environmentally sustainable waste disposal is an obligation defined by the European Union directives (1999/31/EC; 2010/75/EU). At the same time, agricultural residues are valuable resources for the realization of the 20-20-20 objectives (2009/28/EC).

The choice of the conversion process depends on type, properties, and quantity of available biomass, on preferred final energy form, environmental standards, and economic conditions. Biomass can be converted into three main products: energy for heating, transport fuel, and chemical raw materials (Saxena *et al*., 2009). Due to being renewable and environmentally friendly (Hossain *et al*., 2010), biofuels from biomass are considered to be the most promising alternative fuel sources. In terms of energy, the most important biomass properties include: proximate analysis (content of moisture, volatile matter, fixed carbon and ash), ultimate analysis (carbon, hydrogen, nitrogen and sulphur contents) and heating value (Imam and Capareda, 2012). The utilization of renewable energy sources is becoming increasingly important in the light of its potential for lowering the global warming effects and for fuel supply (Cuiping *et al*., 2004). Namely, in complete biomass-fired fuel combustion the only by-products are Carbon dioxide (CO_2) and water (H_2O), while incomplete combustion generates health damaging gases and GreenHouse Gases (GHG), such as Carbon monoxide (CO), Nitrogen dioxide (NO_2), methane (CH_4), Polycyclic Aromatic Hydrocarbons (PAH), etc. (Bhattacharya and Salam, 2002). When compared to coal, biomass has lower contents of sulphur and ashes. In some cases, biomass fuels have a high nitrogen content that can result in rather high NO_x emissions (Klason and Bai, 2007; Van den Broek, 2000).

The investigation of energy potential of pruned biomass from different fruit trees and grapevine should be carried out in time of mature pruning, because, due to its substance, biomass from green pruning is poor in energy properties. Orchards and vineyards require pruning on an annual basis, generating large amounts of biomass, which may be utilized as a source of bioenergy. Because of their properties and quantities, the residues of mature pruning are very interesting as a source of bioenergy (Radojevic *et al*., 2007a; Scarlat *et al*., 2010). Furthermore, fruit industry waste, which is a part of food processing waste, was selected for this study because of its suitability for combustion (Kaynak *et al*., 2005). It is well known that high quality and active adsorbents are produced from some biomass resources such as agricultural shells, husks, and pits (Vassilev *et al*., 2010). These sorts of waste are suitable for energy combustion, because of very low moisture content and the fact that they do not contain any hazardous compounds, like chloride. Their calorific values are similar to those of wood because pits (stones) have a high lignin content (Kaynak *et al*., 2005).

Plum (*Prunus domestica)* is a fruit specie which is presently grown in many European and world areas. It is noticeably widespread in Croatia as well; according to the Statistical Yearbook of the Republic of Croatia (2010), plum is the third most grown fruit species. Di Blasi *et al*. (1996), Radojevic *et al*. (2007b), and Bilandzija *et al*. (2012) assert that on average 2.63 tons of pruned biomass per hectare remain after pruning on permanent plantations. Moreover, plum fruit consists of flesh and stone in an average ratio of 95%:5% (Sic Zlabor *et al*., 2012). Plum flesh is used in food processing and pharmaceutical industry, while stone and pruned biomass are by-products representing highly valuable biomass of agricultural origin.

Therefore, the goal of this study was to determine proximate, ultimate, and energy values analysis of biomass generated from pruning and processing of plum fruit. We also aimed to analyse and compare five different plum varieties (Bistrica, Čačanska ljepotica, Čačanska rodna, President and Stanley), which represent varieties most commonly grown in the Republic of Croatia and, on the basis of the values resulting from this study and data from the relevant literature, investigate the total energy potential of the studied species.

MATERIALS AND METHODS

Materials

The reason for selecting plum fruit as the main raw material for this investigation lies in the fact that, according to the Statistical Yearbook of the Republic of Croatia 2010, this culture is defined as the most widely grown kernel fruit species in the country. It is grown on a total of 4,754 hectares.

The investigation of biomass (pruned biomass and stone) was carried out on five different and most common plum varieties in Croatia i.e., in Vukovarsko-srijemska County. They are Bistrica, Cacanska ljepotica, Cacanska rodna, President, and Stanley. The area of Vukovarsko-srijemska County was selected because it is situated in central part of the Southeast Europe, so that these investigations can easily be implemented in other countries of the region as well. Pruned biomass samples were taken directly after the winter pruning of permanent plum orchards (February, 2012). After harvest (August and September, 2012), pits were separated from plum flesh. The average age of plantations was between five and ten years. Since the Statistical Yearbook of the Republic of Croatia does not contain information on shares of individual varieties, the calculation of energy potential of the residues from plum cultivation and processing was based on literature references which define average quantity of investigated residues, in addition to the analysed average heating value.

Methods

The analytical investigation was conducted in the laboratory of the Department of Agricultural Technology, Storage, and Transport of the Faculty of Agriculture, University of Zagreb.

Before the analysis, all samples were dried up in order to eliminate extrinsic moisture and to enable comparison of samples in identical operative conditions. After drying, samples were ground in a laboratory grinder (IKA Analysentechnik GmbH, Germany). Each sample was analyzed at least three times in order to provide reproducibility of the analyses.

The results will be compared with the data from the relevant literature and with the values set out in the norm CEN/TS 14961 (2005) for solid biofuels.

Proximate Analysis

Samples were characterized by proximate analysis according to standard methods: moisture content (CEN/TS 14774-2: 2009) in laboratory oven (INKO ST-40, Croatia); whereas ash (CEN/TS 14775: 2009), fixed carbon (by difference), and volatile matter (CEN/TS 15148: 2009) were determined by use of muffle furnace (Nabertherm GmbH, Nabertherm Controller B170, Germany).

Ultimate Analysis

Total carbon, hydrogen, nitrogen, and sulfur were determined simultaneously, by method of dry combustion in a Vario Macro CHNS analyzer (Elementar Analysensysteme GmbH, Germany), according to the protocols for determining carbon, hydrogen, and nitrogen (EN 15104: 2011) and sulfur (EN 15289: 2011). Likewise, the oxygen content was calculated by difference.

Heating Value

The heating value was determined by ISO method (EN 14918: 2010) using an IKA C200 oxygen bomb calorimeter (IKA Analysentechnik GmbH, Heitersheim, Germany). 0.5 grams of sample were weighed 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^{-1} on a dry basis.

Statistical Analysis

All data obtained in this way were analyzed according to the GLM procedure in the SAS system package version 8.00 (SAS Institute, 2000).

RESULTS AND DISCUSSION

The authors Mediavilla *et al*. (2009), Khan *et al*. (2009), and Telmo *et al*. (2010) consider these analyzed components as the most important chemical properties of biomass in dry processes of its transformation, which are crucial for the quality of biomass as energy source. Since the norm for energy use of pruned biomass of fruit species has not been defined yet, the obtained results were compared against the values set out by the CEN/TS 14961 (2005) norm for broad-leaf biomass, as the most comparable category within this norm. The data of this Technical Specification were obtained mainly from a combination of the investigations carried out in Sweden, Finland, Denmark and Germany. Unlike pruned biomass of fruit species, the norm sets out values for stone of some fruit species (peach, apricot, cherry and sour cherry). Therefore, the obtained analyses of plum stone were compared with the values set out for stone of the mentioned cultures. The prescribed values resulted from combination of the researches carried out in Austria, Italy, Greece, Spain, and Malaysia. Given the fact that CEN/TS 14961 (2005) prescribes only some parameters analyzed in this investigation (ash content, lower heating value, and C, H, N, O, S content), the results were compared against the relevant literature references.

Proximate Analysis

The proximate analysis typically involves determination of moisture, volatile matter, fixed carbon, and ash, and represents the most frequently used method for biofuel characterization (Thipkhunthod *et al*., 2005; García *et al*., 2012). Table 1 shows the results of the proximate analysis of two types of the investigated biomass, resulting

Table 1. Proximate analysis of investigated pruned plum and plum stone.[a]

Variety/Samples	MC (%)		AC (% db)		FC (% db)		VM (% db)	
	PB	PP	PB	PP	PB	PP	PB	PP
Bistrica	7.10	4.67bc	2.10	1.05a	21.05a	14.07b	69.75c	80.23
Cacanska lepotica	6.87	5.29b	2.01	0.69b	17.86b	11.69d	72.94a	82.33
Cacanska rodna	7.01	4.32c	2.13	0.56b	19.65a	12.79c	71.21b	82.32
President	6.98	4.83b	1.97	0.39c	17.17b	15.19a	73.88a	79.58
Stanley	7.14	5.83a	2.18	0.64b	19.83a	12.22c	70.85b	81.31
Significance[b]	NS	***	NS	***	*	***	***	NS
$\overline{X}$	7.02	4.98	2.07	2.20	19.11	13.19	71.72	81.15

[a] % db= % on dry basis; MC= Moisture Content; AC= Ash Content; CK= Coke; FC= Fixed Carbon; VM= Volatile Matter; PB= Pruned Biomass, PP= Plum Pits. Different letters within a column indicate significant differences at the 5% level. [b] Significance: *** P< 0.001; ** P<0.01; * P< 0.05, NS= Non-Significant.

from five different plum varieties.

In general, moisture can vary considerably in content and is an undesirable ingredient in any fuel. Moisture content influences calorific value, combustion efficiency and combustion temperature (Obernberger and Thek, 2004). Moisture of the investigated pruned biomass varied from 6.98 to 7.14%, while moisture in pits was between 7.54 and 8.65%. Kaynak *et al.* (2005), Atimtay and Kaynak (2008), Demirbas *et al*. (2009), García *et al*. (2012), Bilandzija *et al*. (2012), and Akalin *et al*. (2012) carried out investigations on different types of pruned biomass and different types of fruit stone (including plum fruit) and also found moisture content to be below 10%, which is considered as optimal for biomass combustion.

Ash is one of the most studied properties of biomass, but unfortunately, due to its complexity, it still is not sufficiently understood. Ash originates simultaneously from natural and techno-genic inorganic, organic, and fluid matter during biomass combustion (Vassilev *et al*., 2010). Moreover, ash is an undesirable ingredient of biomass because of its catalytic influence on thermal decomposition; also, a higher concentration of ash results in higher carbon and gas concentrations. The melting point of biomass ash is relatively low and ash melting during thermal process generates "slag". Formation of slag in furnaces or boilers obstructs transference of energy and decreases the combustion efficiency (Hodgson *et al*., 2010). As the norm CEN/TS 14961 (2005) sets out the allowed level of ash at 0.2 to 1.0% (for both types of investigated biomass) it can be asserted that the analyzed pits were fully within the limits set by this norm, with the values between 0.39 and 1.05%. As for the pruned biomass, the analysis was carried out of higher contents of ash in the range from 1.97 to 2.18%. Higher variations in ash content were not unexpected because the data from García *et al*. (2012) determined the percentage content of ash in pruned plum biomass at 6.6%. Also, the same author found ash content of 1.8% in plum stone, while Atimtay and Kaynak (2008) and Akalin *et al*. (2012), who investigated peach and cherry stone, determined ash content of 1.80 and 1.43%, respectively. However, according to National Plan for Research and Technological Innovation of Spain (2007), variations in ash content in biomass are explained by different content of mineral nutrients in soil. Moreover, ash content in biomass also depend on climate conditions of the areas biomass originates from. In general, ash content can be related to average temperatures of the sites from which the samples were taken. However, this should not be considered as a rule.

Fixed carbon refers to carbon in its free state, not combined with other elements (UN, 2006). Fixed carbon produces char and burns as a solid material in the combustion system (Kreil and Broekema, 2010). Thus, high levels of fixed carbon will have a positive impact on combustion properties. High fixed carbon content is a characteristic of herbaceous agricultural biomass residues (Vassilev *et al*., 2010). Fixed carbon levels are expected to be from 7 to 20% (Yao *et al*., 2005). The analyses of pruned biomass revealed that fixed carbon content was between 17.17 and 21.05%, while in pits, the fixed carbon levels were between 11.69 and 15.19%. According to García *et al*. (2012), the percentage of fixed carbon in pruned plum biomass was analyzed at 21.40%, which is somewhat higher than the values found in this investigation. Given the fact that literature references set the percentage content of fixed carbon in different types of fruit pits in a range from 9.47 to 21.20% (Atimtay and Kaynak 2008; Vassilev *et al*., 2010; Akalin *et al*., 2012; García *et al*., 2012), it can be asserted that there is a relatively wide divergence within the investigated biomass type and that the analyzed stone samples are consistent with the literature references.

Volatile matter in biomass usually includes light hydrocarbons, CO, CO_2, H_2, moisture, and tars (Demirbas, 2004; Vassilev *et al*., 2010). In general, the volatile matter is high in biomass, with values of about 75%, potentially increasing up to 90%, depending on the raw material (Khan *et al*., 2009). In the investigated biomass, the volatile matter content varied in the interval of 69.75 to 73.88% for pruned biomass, while limit values for the analyzed pits were between 75.76 and 79.70% and was in an expected range. This is confirmed as well by the investigations by Vassilev *et al*. (2010) and García *et al*. (2012), who have determined volatile matter in pruned plum biomass and pits at 74.6% and from 77.0 to 80.8%, respectively.

Ultimate Analysis

The ultimate analysis includes an assessment of the levels of carbon, hydrogen, oxygen, nitrogen and sulphur. Among many biomass properties, contents of energy-carrying chemical bonds between the most abundant ultimate elements, together with total ash content, represent the most important readings (Thipkhunthod *et al*., 2005**;** Tao *et al*., 2012). The results obtained for ultimate analysis of the investigated biomass are shown in Table 2.

Carbon, nitrogen, and oxygen are the main components of solid fuels. Carbon and oxygen react during combustion in an exothermic reaction, generating CO_2 and H_2O; thus, they contribute in a positive way to the fuel's HHV and the combustion process itself (Obernberger and Thek, 2004).

Carbon is one of the most important elements in the combustion process. Favourable carbon content in biomass composition is exceptionally important because its increased presence boosts the heating value of biomass (Obernberger and Thek, 2004). Comparison of the values set out in CEN/TS 14961 (2005) for carbon (48-52% for prune biomass; 51-55% for fruit stone) with the values found in this investigation (49.07- 52.11% in pruned biomass; 52.11- 55.29% in fruit pits) shows that the latter are fully consistent with the prescribed levels. Moreover, the consistency of the analyzed data is evident when they are compared with the investigations conducted by Garcia *et al*. (2012) on pruned biomass of apple, almond, apricot and cherry. These investigations determined the level of carbon between 43.25 to 59.59% while Atimtay and Kaynak (2008) and Akalin *et al*. (2012) determined it between 46.44 to 52.38% in peach, apricot, and cherry stone.

Reduced hydrogen content may represent a problem because, together with carbon, hydrogen is essential for determining energy properties of solid biofuels (Obernberger and Thek, 2004). The investigations described in this paper looked into percentage shares of hydrogen of 6.07 to 6.74% (for pruned biomass) and 6.21 to 6.94% (stone). Since the norm CEN/TS 14961 (2005) prescribes

Table 2. Ultimate analysis of investigated pruned plum and plum stone.[a]

Variety /Samples	C (% db)		H (% db)		O (% db)		N (% db)		S (% db)	
	PB	PP	PB	PP	PB	PP	PB	PP	PB	PP
Bistrica	48.15	54.64	6.50	6.80	44.35	37.75	0.84	0.76b	0.17	0.042
Cacanska lepotica	47.48	55.29	6.21	6.32	44.07	36.77	0.74	1.60a	0.16	0.044
Cacanska rodna	49.07	54.61	6.07	6.27	44.85	37.81	0.79	1.33a	0.16	0.045
President	47.97	52.11	6.74	6.94	44.72	40.59	0.85	0.36c	0.18	0.038
Stanley	48.85	53.45	6.64	6.72	44.82	39.45	0.91	0.81b	0.17	0.039
Significance[b]	NS	NS	NS	NS	NS	NS	NS	***	NS	NS
$\overline{X}$	48.30	54.02	6.43	6.61	44.48	38.47	0.82	0.97	0.16	0.041

[a] C= Carbon; S= Sulphur; H= Hydrogen; O= Oxygen; N= Nitrogen; % db= % on dry basis; PB= Pruned Biomass, PP= Plum Pits. Different letters within a column indicate significant differences at the 5% level. [b] Significance: *** $P< 0.001$; ** $P<0.01$; * $P< 0.05$, NS= Non-Significant.

the value of hydrogen at 5.9 to 6.5% for pruned biomass and 5 to 7% for fruit stone, it is evident that the analyzed values are within the range of the prescribed limits. Also, the comparison of the analyzed values in this paper with the literature references allows to observe the consistency of the data shown here. Namely, data from literature indicate the hydrogen content in pruned biomass of 6.21 to 11.55% (grapevine, cherry, apple, apricot) and 5.99 to 6.70% in fruit stone (cherry, apricot, plum, peach) (Garcia *et al*., 2012; Akalin *et al*., 2012; Atimtay and Kaynak, 2008; Vassilev *et al*., 2010). Garcia *et al*. (2012), comparing carbon with hydrogen, assert that the former is a significant element in terms of its influence on energy value of biomass. The investigated values corroborated this thesis, which can also be observed by comparing hydrogen against the analyzed energy values in this study.

An acceptable level of oxygen is a crucial parameter in biomass, because of the negative impact this element has on the fuel performance. Namely, oxygen binds a part of combustion elements (carbon, hydrogen) and lowers heating value of biomass. However, it also causes flame elongation because it dilutes the hydrocarbons that are separated, and ultimately leads to lowering the quantities of char in furnaces (Van Loo and Koppejan, 2010; Vassilev *et al*., 2010). In this study, oxygen content was between 44.07 to 44.85% (in pruned biomass) and 36.77 to 40.59% (in fruit stone). Since CEN/TS 14961 (2005) sets out oxygen content at 41 to 45% for pruned biomass and 43% for fruit stone, there is evident consistence of the data found in the analyses of pruned biomass, while the analysis of fruit stone found a content which is below prescribed level. Comparing the obtained data with literature references regarding fruit stone, inconsistence with the applicable norm can be observed. Namely, the oxygen content in apricot, plum, and peach stone is below the values of literature data (38.78-42.40%), but higher in cherry stone (Atimtay and Kaynak, 2008; Vassilev *et al*., 2010; Garcia *et al.,* 2012, Akalin *et al*., 2012).

Also, since nitrogen content, together with sulfur, influences the emissions of harmful gases (NO_x and SO_2) during biomass combustion (Sáez Angulo and Martínez García, 2001; Garcia *et al*., 2012), concentrations of these gases should be as low as possible. Sulfur is a gas with the lowest presence in biomass, but, together with nitrogen are the most important elements regarding the environmental impact. Investigation in nitrogen and sulfur content determined their respective levels in pruned biomass (0.74-0.91% and 0.16–0.18%, respectively) and in plum stone (0.36-1.60% and 0.03–0.04%, respectively). The norm applied in this investigation prescribes maximum allowed limits for nitrogen and sulfur for pruned biomass at 0.1-0.5% and 0.01-0.05%, respectively, and for fruit stone at 0.2-0.3% and 0.05-0.5%, respectively. In both investigated biomass groups, these elements somewhat diverged from these values, except for sulfur levels in the analyzed stone samples, which is fully consistent with the norm. However, based on the insight in the literature data, the mentioned divergence from the norm could be expected. Namely, Garcia *et al*. (2012) , Atimtay and Kaynak (2008), and Vassilev *et al*. (2010) determined the nitrogen and sulfur content in pruned biomass of cherry, grapevine, and apple (0.52–0.81%; 0.17-0.46%, respectively) as well as their content in plum, apricot, and peach stone (0.52–0.81%; 0.17-0.46% respectively).

However, the use of biomass as a fuel for thermal and electrical applications requires knowledge of its heating value. Heating value reflects the energy content of a fuel in a standardised fashion. It is often expressed as higher heating value or lower heating value. Higher heating value refers to heat released by complete combustion of a unit volume of fuel leading to the production of water vapour and its eventual condensation; at this point, the total released energy is measured. Lower heating value does not contemplate this latent heat of water contained by fuels (Vargas-Morenoa *et al.,* 2012). The results obtained for heating value analysis for the investigated biomasses are shown in Table 3.

The higher heating values for plum pruned biomass were between 18.36 and 18.71 MJ kg^{-1}, while for investigated stone, they were between 17.00 and 17.29 MJ kg^{-1}. Thus, it is possible to establish that there are no significant variations between different varieties. Also, lower heating values for pruned biomass were between 16.42 and 17.29 MJ kg^{-1}, while in stone they were between 14.07 and 16.24 MJ kg^{-1}. Based on the values prescribed in CEN/TS 14961 (2005) (pruned biomass: higher heating value 19.4–20.4 MJ kg^{-1}; lower heating value 18.4–19.2 MJ kg^{-1}; fruit stone: higher heating value 19.0–20.0 MJ kg^{-1}; lower heating value 17.5–19.0 MJ kg^{-1}), it can be observed that the analyzed values were lower than prescribed in both types of the investigated biomass. However, a comparison with the data found by Atimtay and Kaynak (2008), Akalin (2012), and Garcia *et al*. (2012) who found higher heating values for pruned biomass from apple, plum and grapevine (16.81-17.82 MJ kg^{-1}), as well as cherry, plum, and peach stone (15.85–20.39 MJ kg^{-1}), shows certain consistence of the data analyzed in this paper. Also, despite some divergence from the data, the investigated biomass still represents highly valuable raw material for the direct production of heat and electricity.

Energy Potential of Investigated Biomass in Croatia

Regarding the investigations which were carried out by Di Blasi *et al*. (1996), Radojevic *et al*. (2007a), and Bilandzija *et al*. (2012), and taking into account different varieties, cultivation forms and age of plantations, it can be concluded that, on average, 2.63 t/ha of pruned biomass remain after pruning of permanent plum plantations. Furthermore, in order to calculate the quantity (t ha^{-1}) of other types of the investigated biomass (stone), the data published by Blagojevic *et al*. (2006) and Sic Zlabur *et al.* (2012) were used. Namely, based on the most commonly used plum shape (V-spindle and Spindle system), Blagojevic *et al.* (2006) determined an average yield (which occurs in the fifth and sixth year of cultivation) of different varieties (Cacanska ljepotica, Stanly, Cacanska rodna, President, Cacanska najbolja) to be 21.08 t ha^{-1}, while Sic Zlabor *et al*. (2012) having analyzed different varieties (Cacanska ljepotica, Stanly, Cacanska rodna, President) determined an average fruit to stone ratio of 95%:5%. According to the yields in Croatia, we could expect that the average yield of 5.1 tons of stone remains per one hectare. On the basis of statistical data on areas under plum plantations in the Republic of

Table 3. Heating values of investigated pruned plum and plum stone.[a]

Variety /Samples	HHV (MJ kg^{-1})		LHV (MJ kg^{-1})	
	PB	PP	PB	PP
Bistrica	18.67	19.09a	17.24	16.42a
Cacanska lepotica	18.48	16.93b	17.02	14.26b
Cacanska rodna	18.36	16.82b	17.00	14.16b
President	18.57	16.76b	17.07	14.07b
Stanley	18.71	18.89a	17.29	16.22a
Significance[b]	NS	***	NS	***
$\overline{X}$	18.55	17.69	17.12	15.02

[a] HHV= Higher Heating Values, LHV= Lower Heating Values; PB= Pruned Biomass, PP= Plum Pits. Different letters within a column indicate significant differences at the 5% level.
[b] Significance: *** $P< 0.001$; ** $P< 0.01$; * $P< 0.05$, NS= Non-Significant.

Table 4. Available quantity and energy potential of plum pruned biomass and stone in the Republic of Croatia.

		Average availability of biomass (t ha^{-1})	Source	Quantity of available biomass (t)	Energy potential (MJ)
Plum[a]	PB [a]	2.63	(Di Blasi *et al*. 1996; Radojevic *et al*. 2007[2]; Bilandzija et. al. 2012)	12,508	214.13
	PP [b]	1.05	(Blagojevic *et al*. 2006; Sic Zlabor *et al*., 2012)	4,992	78.0
Total					292.13 MJ

[a] Pruned Biomass, [b] Plum Pits.

Croatia (4,754 ha) and average available quantities of both investigated types of biomass, total potential of available biomass was calculated (17,500 tons per year). Based on the energy values shown in Table 3, it can be determined that for both investigated types of plum biomass there were no significant differences among the varieties. Therefore, calculation of energy potential was based on average lower heating value (pruned biomass 17.12 MJ kg^{-1}, stone 15.02 MJ kg^{-1}) of the investigated varieties.

Regarding the heating values of some fossil energy sources (lignite 20.20 MJ kg^{-1}, coal 27.60 MJ kg^{-1}, coke 29.50 MJ kg^{-1}, heating oil 41.5 MJ kg^{-1}), the ratios of the investigated biomass (pruned biomass 17.12 MJ kg^{-1}, stone 15.02 MJ kg^{-1}) to these fossil fuels can be determined. They are as follows: ratios of pruned biomass to lignite, coal, coke, and heating oil are 1: 1.17; 1.61; 1.72, and 2.42 respectively, while for plum stone they are 1: 1.34; 1.83; 1.96; and 2.76 respectively. These ratios indicate that the energy potential of the investigated biomass types is high and that they provide clear environmental benefits when it comes to biomass combustion and disposal. Also, following the Energy Development Strategy of the Republic of Croatia (Official Gazette 130/2009), Croatia has set a target of using 26 PJ of energy from agricultural and forestry sources by 2020, and the investigated types of biomass (pruned biomass from permanent plantations and stone-fruit pits) can contribute to achieving this goal.

CONCLUSIONS

On the basis of the investigations of energy potential of pruned biomass and stone of five plum varieties (Bistrica, Cacanska ljepotica, Cacanska rodna, President and Stanley), it can be concluded that: The analyzed values of combustible and non-combustible matters showed that the use of plum stone and pruned plum biomass as a source of biofuel is sustainable. It can be determined that variety does not influence combustible and non-combustible properties of stone and pruned biomass. Based on lower heating values and quantities of pruned biomass and plum stone, the energy potential of this resource in Croatia is calculated at 292.13 MJ. Given the acceptable level of sulfur in the investigated samples, the observed plum stone and pruned biomass can be characterized as an ecologically acceptable biofuel whose energy use, especially by small consumers in the areas where fruit industry is well developed, might reduce the consumption of fossil fuels and brings additional economic savings and social benefits.

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تجزیه اجزا و تجزیه نهایی و تعیین ارزش انرژی زیست توده محصولات جانبی آلو: مطالعه موردی در کروواسی

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چکیده

در بسیاری از کشورهای اروپایی، پسمانده های محصولات کشاورزی منبع مستعد و قابل توجهی برای توسعه صنعت انرژی زیستی قلمداد می شوند.بخش قابل توجهی از این مواد زیست توده از فعالیت های پرورش میوه از جمله فعالیت های تولید میوه و کارخانجات فرآوری این محصولات به دست می آیند.دستورالعمل های اتحادیه اروپا الزام می کند که دورر یختن این پسماندها به گونه ای باشد که با پایداری محیط زیست سازگار باشد. هدف پژوهش حاضر تجزیه اجزای این مواد(رطوبت موجود، خاکستر، کربن تثبیت شده،و مواد فرآر) و تجزیه نهایی (کربن، هیدروژن، نیتروژن و سولفور) و ارزش انرژی (بالاتر، پایین تر) مواد زیستی مزبور ونیز تعیین استعداد و پتانسیل کلی انرژی درکروواسی بعد از انجام هرس(پسماند هرس درختان) و انجام فرآوری میوه های آلو(هسته میوه) بود. به این منظور پنج رقم آلو(شامل بیستریکا،کاکانسکا لجپوتیکا، کا کانسکا رودنا، پرزیدنت ، و استانلی) که کاشت آن ها در کروواسی رایج است مورد تجزیه و مقایسه قرار داده شد. نتایج این تجزیه ها با نورم های(2005) CEN/TS 14961 برای زیست سوخت های جامد و داده های منابع علمی مربوط مقایسه شد. در نتیجه، اثبات شد که هر دو نوع زیست توده مطالعه شده منابع بسیار ارزشمندی برای انرژی بودند و هیچگونه تفاوت معنی داری بین رقم های مختلف آلو مشاهده نشد. گفتنی است که میانگین ارزش حرارتی پایین تر(که از پارامترهای عمده کارآیی انرژی زیست توده قلمداد می شود) در نمونه های بررسی شده عبارت بود از: ۱۵/۲ مگاژول در کیلو گرم برای هسته و۱۷/۲ مگا ژول در کیلو گرم زیست توده هرس شده. این داده ها نشان می دهد که می توان آلو را به عنوان یک ماده خام ارزشمند برای تولید انرژی در نظر داشت. همچنین، محاسبات نشان می دهد که استعداد تولید سالانه زیست توده در کروواسی از طریق انرژی "سبز" تجدید پذیر، می تواند به۲۹۲/۱۳ مگا ژول برسد.

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