Fuel Properties' Comparison of Allochthonous *Miscanthus* x *giganteus* and Autochthonous *Arundo donax* L.: a Study Case in Croatia

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Summary

Increased energy demands, EU intentions for energy independence, together with decreasing fossil fuel reserves, have initiated the interest for new technology development. This would enable more intensive use of new renewable energy sources and contribute to increase among appliances based on biomass and energy crops. *Miscanthus x giganteus* is a perennial crop which has been received particular attention during the last decade as an energy crop. In the Republic of Croatia, it has been under investigation for the last two years, and the yields obtained by far are very promising. However, due to its potential and autochthonicity, there is a need for investigating the potential of another perennial, *Arundo donax* L. as energy crop. Among numerous tested energy crops, both species seem to be especially promising feedstocks due to their high production potential. Cultivation of these plants may be a sufficient alternative to wood from short-rotation forestry. Therefore, the objective of this study was to determine fuel properties of the two-abovementioned species, relevant for combustion of biomass to be used as solid fuel, and to compare them. Since biomass is characterized by a series of parameters that determine their most suitable process of conversion, properties such as biomass type, particles size, chemical and physical composition, way of fixation of the moisture, ash content, and higher heating value (HHV). Accordingly, proximate, and ultimate analyses, together with fuel properties determination were conducted on both, *M. giganteus* and *A. donax* Results indicated that both species could be proposed as biomass energy crops in the Republic of Croatia, with a significant and environmentally compatible contribution to energy needs.

Key words

Miscanthus x giganteus, *Arundo donax* L., energy crop, fuel properties

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Introduction

Biomass utilization on a global scale could contribute to environmental protection, having in mind that biomass sources are CO_2-neutral. Biomass utilization is also one of the key tools to reduce dependence on imported oil and oil products, thus improving the security of energy supply (Krička et al., 2007; Krička, 2009). Several biomass feedstocks for energy can readily be produced in the EU, such as those from arable crops currently grown for food: sugar, starch and oil crops, forestry or domestic waste, and marine biomass. However, it is also possible to increase the production of dedicated crops, the energy crops that are bred or selected to produce biomass with specific traits that favour their use as an energy vector (Mantineo et al., 2009).

One of the most promising sources of biomass are lignocellulosic crops that can be used for production of heat and electricity by means of direct combustion or by production of biofuel and biogas. Those are already well-known technologies. Biomass can be converted through different processes into solid (e.g., powder, briquettes, cubes, and pellets), liquid (bioethanol, propanol, and butanol *via* cellulose process), and gaseous (e.g., methane *via* anaerobic digestion) fuels (Rosillo-Calle et al., 2007; Lal, 2008; Scott et al., 2010). The design or choice of the processes has to be based on the biomass properties that include physical characteristics such as calorific value, and chemical ones, such as content of carbon, hydrogen, oxygen, nitrogen, sulphur, and ash (Tao et al., 2012). These properties may vary considerably with species (Christian et al., 2006), growing environment (Xiong et al., 2010), management (Landstrom et al., 1996; Lewandowski and Kauter, 2003), and delayed harvest period (Lewandowski and Heinz, 2003). Differences in biomass properties or feedstock quality between species can be largely attributed to the nature of the plant that is determined by its physiology and evolution. Identifying these differences and/or similarities in association with species is absolutely necessary. Without this knowledge, it would be impossible to perform basic studies on the mechanism behind the variations and therefore to improve the predictability of biofuel characteristics and/or to manage feedstock production (Tao et al., 2012). Due to EC advisories, a maximum of 30% of potentially available biomass can be used for energy production (Tomić et al., 2011).

Research carried out in recent years in the Mediterranean environment, where the constraints are low water availability and high temperatures during summer, have indicated that *Arundo donax* L. and *Miscanthus* spp. are among the most promising species for energy production (Lunnan, 1997; Christian and Haase, 2001; Lewandowski et al., 2000; Mantineo et al., 2009). These unimproved perennial species produce considerable amounts of lignocellulosic biomass; they are either naturalised in Mediterranean area (*A. donax*) or have good adaptation capacity (*M. giganteus*) in these environments (Mantineo et al., 2009). Therefore, objective of this research was to determine fuel properties of the *M. giganteus* and *A. donax* biomass, harvested in the period of their maximum yield, relevant for direct combustion of biomass and energy production.

Materials and methods

Materials

M. giganteus biomass, used for the purpose of this investigation, was harvested at two locations, Ličko Petrovo Selo (44° 52′ 48.87″ N, 15° 42′ 42.44″ E) (sample LPP) and Zelina Breška (45° 41′ 24″ N, 16° 24′ 0″ E) (sample ZB), on lower quality soils, in a regime of low agricultural investments. Harvest was carried out in October 2013 due to high yield availability. *A. donax* biomass, also used for the purpose of this investigation, was harvested at three locations, Orašac (42° 42′ 7″ N, 18° 0′ 24″ E) (sample OR), Brgat (42.646596°N, 18.161252°E) (sample BR), and island of Pag (44° 29′ 0″ N, 14° 58′ 0″ E) (sample PA) on lower quality soils. Harvest was carried out in November 2012.

Before the analysis, samples were dried until extrinsic moisture was eliminated, so comparison of samples was possible in the same operative conditions. After drying, samples were ground in a laboratory grinder (IKA Analysentechnik GmbH, Germany). Each sample was analysed at least three times to provide reproducibility of the analyses. The obtained data are further presented in tables, together with standard deviation (SD).

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 using muffle furnace (Nabertherm GmbH, Nabertherm Controller B170, Germany).

Ultimate analysis

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

Calorimetry

Heating value was determined by ISO method (EN 14918:2010) using an IKA C200 oxygen bomb calorimeter (IKA Analysentechnik GmbH, Heitersheim, Germany). A total of 0.5 g of sample was 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 on dry basis.

Statistical analysis

All data obtained in this way were analysed according to the GLM procedure in the SAS system package version 8.00 (SAS Institute, 1997).

Results and discussion

Proximate analysis

Proximate analysis is the most frequently used method for biofuel characterization; it is defined as the determination of moisture, ash and volatile content in biomass samples (García et al., 2012). Table 1 shows the results of proximate analysis of two types of investigated biomass, harvested at different locations.

Table 1. Proximate analysis of *M. giganteus* and *A. donax* grown at different locations

Location	MC, %	AC, % db	CK, % db	FC, % db	VM, % db
			Miscanthus x giganteus		
LPP	46.34bc±2.31	1.37b±0.16	11.42b±0.18	10.05b±0.22	89.81b±0.002
ZB	43.27c±1.15	1.65b±0.24	11.91b±1.55	10.25b±1.72	89.57b±0.02
			Arundo donax L.		
OR	46.91ab±1.68	1.40b±0.25	8.57c±0.34	7.17c±0.09	92.73a±0.001
BR	49.45a±1.61	2.33a±0.25	14.12a±0.12	11.79a±0.13	87.93c±0.001
PA	48.14ab±1.47	2.43a±0.33	12.42b±0.27	9.99b±0.06	89.75b±0.001
Significance	0.0122*	0.0007***	<0.0001***	0.0004***	0.0003***

MC = moisture content; AC = ash content; % db = % on dry basis; CK = coke; FC = fixed carbon; VM = volatile matter; significance: *** $p<0.001$, ** $p<0.01$, * $p<0.05$

Table 2. Ultimate analysis of *M. giganteus* and *A. donax* grown at different locations

Location	C, % db	S, % db	H, % db	O, % db	N, % db
			Miscanthus x giganteus		
LPP	49.75a±0.24	0.08d±0.001	4.06b±0.03	45.68d±0.17	0.43c±0.11
ZB	49.31b±0.08	0.08e±0.002	3.98c±0.07	46.41b±0.01	0.22d±0.03
			Arundo donax L.		
OR	49.43b±0.001	0.12b±0.001	4.18a±0.001	45.78d±0.001	0.49c±0.001
BR	49.06c±0.001	0.11c±0.001	4.03bc±0.001	46.17c±0.001	0.63b±0.001
PA	47.62d±0.001	0.14a±0.001	3.88d±0.001	47.10a±0.001	1.26a±0.001
Significance	<0.0001***	<0.0001***	<0.0001***	<0.0001***	<0.0001***

C = carbon; S = sulphur; H = hydrogen; O = oxygen; N = nitrogen; % db = % on dry basis; significance: *** $p<0.001$, ** $p<0.01$, * $p<0.05$

Details of Table 1 show that the studied samples of both, *M. giganteus* and *A. donax* had moisture contents somewhat below 50%, which was similar to those found by Bilandzija et al. (2013) for *Miscanthus* species, and Angelini et al. (2005) for *Arundo* species. Moisture content has an influence on the calorific value, the combustion efficiency, and the temperature of combustion (Obernberger and Thek, 2004). Hence, it is critical in incineration, gasification, and pelletization processes. Freshly harvested hardwoods, softwoods, and herbaceous materials typically have moisture contents of 40% to 65% (Roos, 2004).

Ash is one of the most studied characteristics of biomass, but unfortunately with the poorest understanding. The complex character of this parameter is the reason for such a problem because ash originates simultaneously from natural and technogenic inorganic, organic, and fluid matter during biomass combustion (Vassilev et al., 2010). From Table 2, it can be seen that analysed samples had ash contents between 1.3% and 2.5%. These values are lower than those found in the bibliography for *Miscanthus* (García et al., 2012), or *Arundo* (Jeguirim and Trouvé, 2009; Vassilev et al., 2010) species. Since ash content is negatively correlated to the calorific value, and its composition can largely affect performance of biomass conversion processes (Channiwala and Parikh, 2002; Tao et al., 2012), low ash levels are desired.

Volatile matter of biomass commonly includes light hydrocarbons, CO, CO_2, H_2, moisture, and tars (Demirbas, 2004; Vassilev et al., 2010). In investigated biomass, volatile matter content varies in the interval of 88% to 93%, and follows the generally expected range (García et al., 2012). High volatile matter content indicates that during combustion most of the biomass materials will volatilize and burn as a gas in the system.

From Table 1, it can be perceived that the fixed carbon content in *M. giganteus* biomass is around 10%, whereas for *A. donax* it varies in the interval of 7% to almost 12%. The high fixed carbon content is a characteristic of herbaceous agricultural biomass residues (Vassilev et al., 2010). Fixed carbon will produce char and burn as a solid material in the combustion system (Kreil and Broekema, 2010), so high levels effect positively on combustion properties. Furthermore, the results confirm common volatile matter/fixed carbon ratio for biomass >3.5 (Vassilev et al., 2010).

Ultimate analysis

Among many biomass properties, the contents of energy-carrying chemical bonds between the most abundant elements carbon, hydrogen, oxygen, nitrogen, and sulphur, together with the total ash content, present the most important data. Biomass properties vary within species; for energy crops, the variations in fuel properties can be attributed to breeding efforts for achieving high yields and agricultural practice (Tao et al., 2012). The results obtained for ultimate analysis for investigated biomass harvested at different locations 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 higher heating value (HHV) and the combustion process itself (Obernberger and Thek, 2004). From Table 2, it is obvious that samples of both, *M. giganteus* and *A. donax* biomass have carbon and oxygen values in range from 46% to 50%, respectively. Hence, carbon content was within range that can be found in studies of different types of biomass (García et al., 2012), and in studies conducted on *M. giganteus* (García et al., 2012; Bilandzija et al., 2013); however, values for *A. donax* were somewhat higher than those found in literature for *Arundo* species (Jeguirim and Trouvé, 2009), which makes it even better raw material for direct combustion. In both, *M. giganteus* and *A. donax* samples, and regardless of the location, hydrogen content was found to be approximately 4%, which was expected value, thus contributing to the HHV in a small share. However, reduced hydrogen content may represent a problem because hydrogen, together with carbon, is defined as a very important element determining energy features of solid biofuels (Obernberger and Thek, 2004).

During combustion, nitrogen is practically fully converted into gaseous N_2 and NO_x, which presents the main environmental impact of biomass burning process (García et al., 2012). As can be seen in Table 2, nitrogen levels found in both species ranged between 0.2% and 0.6%, respectively; however, *A. donax*, sample PA, expressed somewhat higher content of nitrogen (1.26%). Even though these components are directly related to the nitrogen oxides emissions, values that were found in all samples show contribution to NO_x much lower than from the air, which has a contribution nearly 15 or 20 times higher (García et al., 2012).

Since sulphur, along with nitrogen, is a cause of undesirable emissions (SO_2) during biomass combustion, it is desirable that biomass has as low sulphur content as possible. The average amount of sulphur for both types of investigated biomass, regardless of the location, was found to be around 1%. Considering its potential environmental impact, low sulphur contents are desirable, and they were in accordance with the ones already recorded for *M. giganteus* (Bilandzija et al., 2013), *A. donax* (Jeguirim and Trouvé, 2009), and other types of biomass (Demirbas, 2004).

Calorimetry

Even though comprehensive knowledge of both, proximate and ultimate analyses is highly important for understanding the energy potential of biomass, calorimetry is considered as the most influential one, since it gives the exact data about the heating value of a specific sample (García et al., 2012). Table 3 shows calorific values of investigated types of biomass.

Higher heating value (HHV), defined as a latent heat of the water vapour products of combustion, was found to be approximately 18 MJ kg^{-1} for *M. giganteus* (Table 3), which was in accordance with the prior recorded data (Bilandzija et al., 2013; Collura et al., 2006; Heo et al., 2010; García et al., 2012). For *A. donax*, HHV was found to be 17-17.26 MJ kg^{-1} (Table 3); thus, it was somewhat lower than for *M. giganteus*, but in accordance with the data obtained by Jeguirim and Trouvé (2009) and Zema et al. (2012).

Moreover, heat content, as a very important factor affecting utilization of any material as a fuel, is affected by the proportion of combustible organic components present in it (Kataki and 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). A linear relationship between carbon content and HHV was found in all investigated samples of *M. giganteus* and *A. donax*.

Table 3. Calorific values of *M. giganteus* and *A. donax* grown at different locations

Location	HHV, MJ kg^{-1} db	LHV, MJ kg^{-1} db
	Miscanthus x giganteus	
LPP	18.08a±0.14	17.20a±0.14
ZB	17.88a±0.19	17.02a±0.20
	Arundo donax L.	
OR	17.20b±0.06	16.28bc±0.06
BR	17.26b±0.05	16.39b±0.05
PA	16.99c±0.05	16.14c±0.05
Significance	<0.0001***	<0.0001***

#HHV = higher heating value; LHV = lower heating value; significance: *** p<0.001,** p<0.01, * p<0.05

Conclusion

Study on *Miscanthus x giganteus* biomass, harvested at two locations (Ličko Petrovo Selo, and Zelina Breška), and *Arundo donax* L. biomass, harvested at three locations (Orašac, Brgat, and island of Pag), showed certain variations in amounts of carbon, hydrogen, oxygen, nitrogen, and sulphur, as well as in moisture, ash, coke, volatile matter, and fixed carbon contents, with regard to type of biomass and harvest locations. Among all investigated parameters, and by comparing two investigated types of biomass, it can be concluded that the only difference between species was observed for ash content; in terms that *A. donax* had somewhat higher ash content, which makes it less favourable fuel. However, the obtained values are still below values defined in CEN/TS 14961:2005 norm for solid biofuels, thus it is suitable for direct combustion. Moisture contents in investigated types of biomass were higher, which was due to the harvest time; hence, other harvest periods could be considered. Hydrogen content observed was somewhat below the CEN/TS 14961:2005 norm, but considering higher oxygen levels detected, there should be no significant effect on combustion properties. Both, nitrogen and sulphur contents were low in samples, giving biomass low emissions of NO_x and SO_2. When speaking of calorific values, HHV was found to be in expected range of approximately 18 MJ kg^{-1}.

Having in mind the applicable standard (CEN/TS 14961:2005), it can be concluded that both investigated types of biomass, *M. giganteus* and *A. donax* have good fuel properties, do not have significant environmental impact, and thus are suitable for utilization as raw materials in direct combustion, and production of electricity and/or heat.

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