Contemporary Engineering Sciences, Vol. 9, 2016, no. 31, 1535 - 1546
HIKARI Ltd, www.m-hikari.com
https://doi.org/10.12988/ces.2016.68136

Biomass Use Best Practices: Monitoring Biomass and Process Emissions for Sustainable Use: A Case Study

Marco Fellin and Martino Negri

CNR-IVALSA
National Research Council - Trees and Timber Institute
via Biasi 75 - 38010 S. Michele all'Adige (TN)- Italy

Daniele Antolini, Paolo Baggio and Elisa Pieratti

Department of Civil and Environmental Engineering
University of Trento
Via Mesiano 77, 38123 Trento, Italy

Abstract

The monitoring solid pollutants, moisture and gaseous emissions of wooden biomass utilized in a 30 kW stove have been performed. This paper reports a case study where the control of organic pollutants in biomass was performed by using FT-IR-ATR technology, heavy metals were measured with ED-XRF, radiation was assessed with a pocket Geiger device. Moisture content has been monitored according to the standard EN 14774-2 and exhaust emissions with a MRU Optima 7 analyzer. The analyses showed no concern about organic pollutants, heavy metals or radiation. The moisture content of some biomass specimen was found very high. The gaseous emissions varied with the use of wet biomass or different part of the tree. This work is a part of the BiQueen project funded by Fondazione Caritro.

Keywords: Biomass, organic pollutants, heavy metals, ED-XRF, radiation, moisture content, gaseous emission

1 Introduction

Biomass utilization is an ever-trending process that is globally used for heating, cooking and energy production purposes. A wide variety of technologies are used, ranging from domestic open fireplaces to complex industrial biomass steam turbines. Although the use of biomass in substitution of petrol-derived fuels is globally desirable due to its sustainable nature and effective role in carbon dioxide atmospheric sequestration [3, 4, 5, 11, 19, 20], many environmental concerns are rising about the use of biomass [1, 23, 24, 25, 26, 27, 28, 29, 34]. Biomass itself can be polluted by organic compounds, heavy metals or even radioactive isotopes. The biomass utilization processes (e.g. open fireplace, efficient stove, gasification...) are emitting potentially dangerous fumes. In addition, the use of wet biomass can lead to worsen this scenario, increasing the pollution emitted versus energy production ratio.

This article summarize experimental and traditional methodologies to assess the quality of biomass and monitor the biomass process outputs. In detail the biomass organic pollutants, heavy metals, radiation, moisture, gaseous emissions were evaluated.

The organic pollutants detection may be achieved by using Fourier Transformed Infrared Attenuated Total Reflectance spectrophotometer (FT-IR-ATR). The FT-IR-ATR technology is a common non-destructive method of chemical analysis, constituted by a fast (less than 1 minute), reliable, relatively cheap (15 000 ÷ 20 000 €), portable (5-10 kg) equipment. The current set-up of the machine allows to manage commercial data-bases and even to build proprietary dedicated data-bases, and to compare the acquired spectra with those of the mentioned records. It also allows to carry out quick test processes for classifying the unknown spectrum in or out a given category. This technology has been previously used also for the classification of wooden waste [36, 37] and on biomass [13].

Biomass elementary composition is usually monitored using Atomic Absorption Spectroscopy (CV, GF, or HG-AAS) or Inductively Coupled Plasma Spectrometry (ICP-OES, ICP-MS) (EN15297, EU Commission decision 2009/894/EC). These methods however require the preparation of the specimen, and therefore are time consuming and somehow expensive, and their preparation process may introduce other variables into the system. Other measurement methods are generally allowed after validation.

The elementary analysis targeted to the heavy metals detection on wood or biomass can be performed by using a handheld ED-XRF device (X-Ray Fluorescence Energy Dispersion). This technology allows on-site analyzes of the chemical elements with atomic number higher than 12 (magnesium) with good accuracy and speed. The instrument is a X-MET 5100 Oxford Instruments in-deep tested and optimized [14, 15, 16, 17, 30] for the use on wooden materials.

The radiation of a material is normally determined by using the gamma spectroscopy technique, which allows the detection of low levels of radiation together with the identification of the isotope(s). Despite being very effective, this technique requires expensive laboratory equipment, cannot be performed on-site and it requires a few hours of measurement time per specimen. Following the Fukushima Daiichi nuclear disaster in 2011, a new generation of low-cost, fast response device has been developed. This device, named “pocket geiger”, is capable of detecting gamma and beta radiations and it is certified by the Dutch Metrology institute. The device can be used on-site and in laboratory. Although the device does not identify isotopes, it can easily be used for quantification of natural background radiation, and therefore for evaluating any radiation which exceed that level.

The biomass moisture content is a key parameter for determining the efficiency of biomass plants and it has a strong influence on the pollutant emissions, together with the type of wood stove adopted [38]. The heat of combustion of a wet biomass (e.g. 40%) can be half of the dry biomass, therefore the produced energy versus pollution emitted ratio and easily get worse with wet biomass in comparison with dry one. According to the technical standard EN 14774-2 the biomass moisture is measured by drying the biomass in a stove and measuring the mass loss with a balance.

Although the recent improvements in the biomass combustion devices technology of the last decades, the number of low-efficiency stoves and boilers that are still in use is greater than the numbers of advanced combustion devices. These apparatus (domestic open fireplaces and traditional stoves) have gaseous emissions ten times higher respect to innovative and automatic wood stoves [5, 22, 29]. In addition, traditional use of biomass residues such as roots, branches, bark (readily available in mountainous or agriculture-based regions) can increase the gaseous emissions [2, 31, 35, 38]. The aim of this work is to evaluate the gaseous emissions from the combustion of different part of the spruce tree, the dominant forest specie in Trentino region (Italy), where this work has been carried on. The combustions and emissions measurements has been carried out in the laboratories of Trento University, Italy, using a high efficiency wood stove. A complete description of the combustion process and emission measurements has been previously published [32, 33].

2 Materials and methods

The organic pollution of biomass was determined by the use of FT-IR-ATR technology. Three spectra from 400 to 4000 cm^{-1} for each of the 77 Norway spruce (Picea abies) wood conditioned in standard environment (20°C and 65% RH) were measured with an Alpha by Bruker Optics GmbH FT-IR-ATR spectrometer equipped with diamond ATR crystal, with resolution of 4 cm^{-1}, 64 scans per sample. Acquired spectra were subjected to processing (via Opus 6.5 software by Bruker) of vector normalization and averaging of replica measures.

These spectra were compared by using a Cluster Analysis (CA) with a database of 145 known pollutants applied to a wood matrix. The known pollutants are the most frequent for biomass operations (mineral oil, unleaded and diesel fuels), and wood industries (coatings, varnishes, glues, laminates...).

The chemical elements present in the fuels were measured by XRF spectrometry (ED-XRF). The X-ray tube was energized with voltage of 45 kV and current of 40 μA. The measurement time of 60 s provided a limit of quantification of the elements compatible with rapid screening for the detection of possible contamination by heavy metals in the biomass, together with the detection of some light elements (e.g. Cl or Ca, with minimum quantification levels of 20000 mg/kg and 300 mg/kg, respectively). Three replica XRF measurements were performed on the 5 types of biomass samples coming from different part of spruce (bark, log, roots, branches, needles...).

The biomass radiation has been measured with a pocket geiger remotely triggered. The biomass and the geiger were placed in a 5 mm thick lead case for the attenuation of natural background. 110 ten minutes measurements on biomass were compared to 70 measurements of background radiation using a one-way ANOVA.

The moisture content of the input biomass (spruce wood chips) was measured following the European Norm (EN) test method EN 14774-2: 2005: drying in an oven at 105 ° C (± 2 ° C) and weighed with a precision balance (0.1 g). Water mass is reported in reference to the wood wet mass. The 7 biomass samples are constituted of 10 portions each, sampled from the stockpile with a shovel. Sampling has been made according to the EN 14778 and the EN 15234.

The experimental combustions has been carried out using a two staged, high efficiency, air wood stove with a thermal output between 11 and 30 kW. The stove works in depression mode and the process is called "reverse flame".

The combustion is adjusted by operating on the exhaust fan or on the supplied air. A lambda sensor measures the remaining oxygen concentration in the flue gas; the stove automatically controls the valves for the inlet of the secondary air to maintain the excess of air at 60%. The stack is equipped with an electrochemical analyzer, MRU compact, in order to measure the gas composition at the chimney (CO, CO2, NO, CxHy, H2, SO2, O2).

3 Results

3.1 FT-IR-ATR

Cluster Analysis (CA) were performed on spectra collected from polluted and not-polluted wood. Differences between contaminated and non-contaminated wood were evident (Fig. 1). CA groups of different pollutants and natural wood were clearly classified in group, with a heterogeneity separation of 70 % and no mis-classifications.

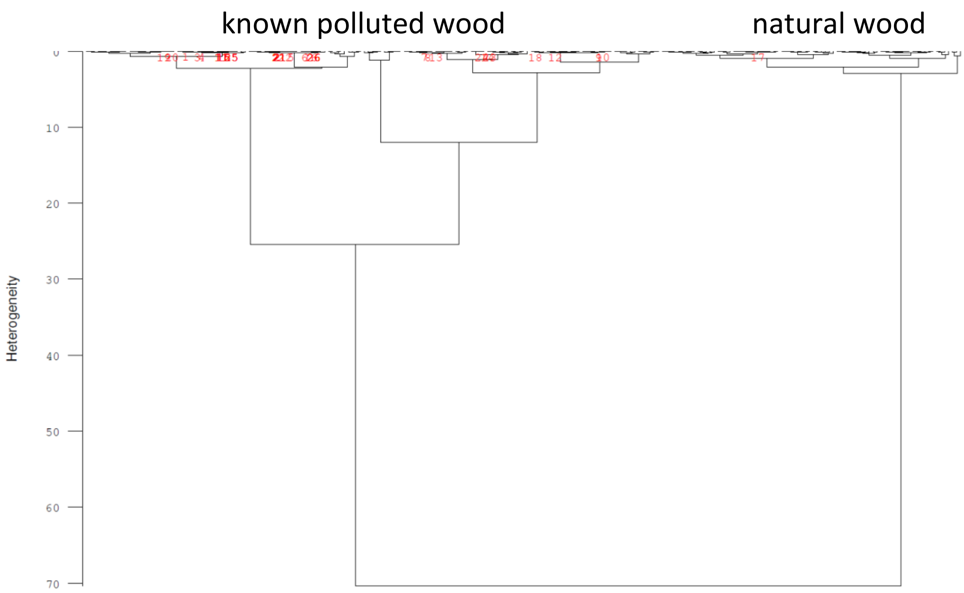

Fig. 1: Cluster analysis of natural wood and contaminated wood.

3.2 Heavy metals content

The results of the elemental analyses in wood chips highlighted the absence of heavy metals. The oligo-elemental analysis showed no concern for heavy metals, and all detected elements are in normal concentrations. The detected elements are presented in Table 1.

[mg/kg]	Ca	Mn	Zn	Sr	Cu
roots	703 (213)	33 (4)	6 (2)	5 (2)	5 (1)
log	475 (123)	14 (5)	6 (0)	3 (0)	6 (1)
bark	5045 (536)	65 (2)	43 (7)	29 (6)	7 (0)
branches	4970 (7629)	201 (229)	37 (50)	24 (30)	7 (3)
needles	5563 (932)	690 (74)	36 (4)	37 (3)	10 (2)

Table 1: ED-XRF elementary measurements of biomass. Average of 3 measurements (and st. dev.)

3.3 Radiation

The radiation of the 110 specimens ranged from 0.030 to 0.077 μSv/h (min, max, respectively). Similarly, the radiation of the 70 natural background measurements ranged from 0.034 to 0.074 μSv/h. The average readings of both biomass and natural background are 0.036 μSv/h, with minimum differences in the standard deviation 0.009 and 0.010 μSv/h for the biomass and the natural background, respectively. The distribution of the measurements is presented in the following histogram (Fig. 2). There were no statistically significant differences between group means as determined by one-way ANOVA ($F(1,176) = 0.49$, $p=0.48$).

No evidence of radiation higher than natural level background can be observed by these measurements.

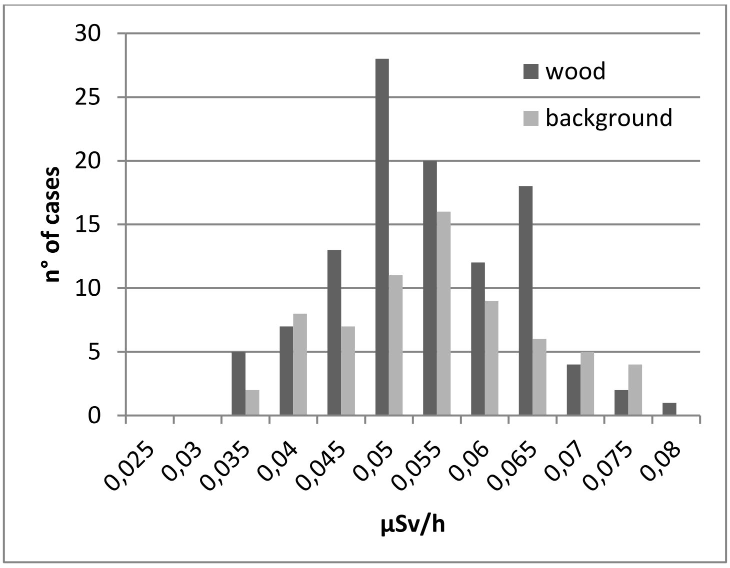

Fig. 2: Radiation of biomass compared with the background radiation

3.4 Moisture content of biomass

The wood chips had a moisture content varying among 8 and 31%. There is an evident increasing of chips moisture content as deep is the sampling point in the chips pile. The surface wood chips are obviously exposed to air and dry faster than the ones placed at few tens of centimeters in depth, which were found to have greater moisture content. Details are presented in the table 2.

Biomass type and sampling place	moisture content UNI CEN 14774-2:2005 %
Wood chips, surface of the pile	8.95
Wood chips, surface of the pile	8.91
Wood chips, 10 cm below surface	12.60
Wood fresh chips 1	31.15
Wood fresh chips 2	29.01
Wood fresh chips 3	28.93
Wood fresh chips, surface of the pile	23.67

Table 2: moisture content of biomass

3.5 Exhaust gas composition

The average values calculated from the data collected during the experimental activity have been converted from ppm to mg/MJ. The calculation of the emission factor for CO, NOx and TOC (Total organic compounds) has been performed according to the standard SFS 5624 (Finnish Standards Association, 1990). The exhaust gas composition has been analyzed and the average values during the stationary combustion phase have been reported in Fig. 3. The SO_2 concentration has not been reported in the table because it is almost zero during the stationary combustion phase.

The results evidence that the wood combustion emissions behave in a very heterogeneous range, since wood has heterogonous composition and each sample is different from the others. The moisture content is confirmed to be very important for NOx concentration which are higher in the emissions from wet wood samples than in others. No evident differences have been noticed in NOx concentrations of the other samples. The CO concentration is below 400 mg/MJ except for three samples. TOC (Total Organic Compound) highest concentration is measured from one of the three "thin branches" replica. Other pretty high values come from one of the two "root" replica and one of the two "dry branches" replica. The other specimens has been found below 5 mg/MJ. Generally, lower emissions have been noticed for "log" samples (bark free).

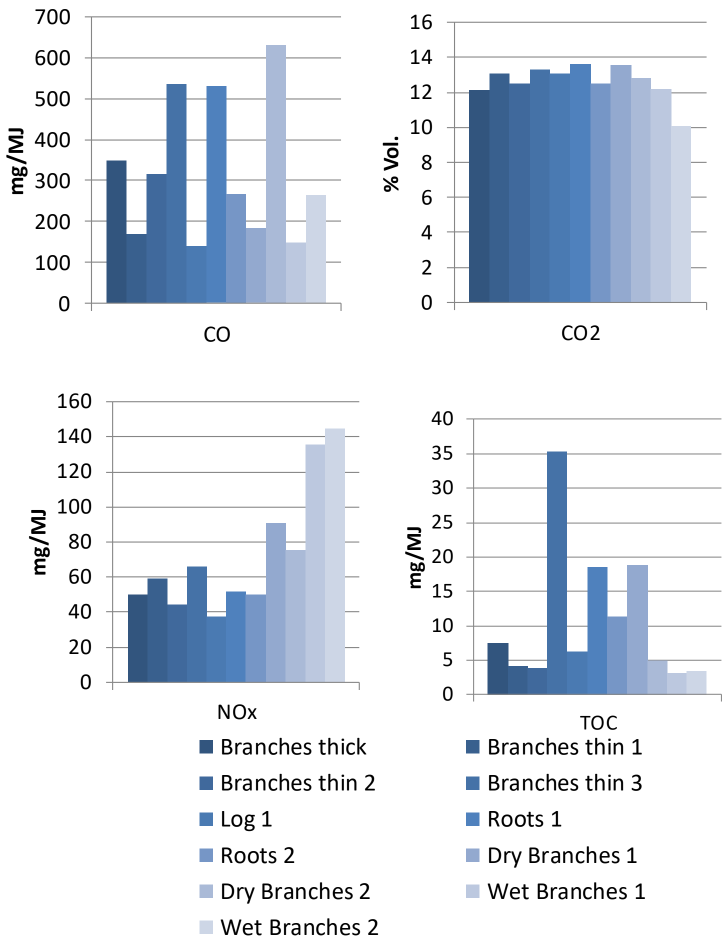

Fig.3 Exhaust gas composition for various biomass types

4 Conclusions

The biomass did not show any presence of organic pollutants and heavy metals content. The biomass radiation showed no difference with the background radiation. The characterization of the different types of biomass resulted in a moisture content partially suitable for combustion (8 ÷ 12%), and partially unsuitable (23 ÷ 31%). A further drying of the least biomass can significantly contribute to improve the overall efficiency of the stove.
The gaseous emissions showed differences in biomass typology, all compliant with the actual emission regulations for these type of stoves.
The used technologies has been proved to be effective in monitoring the biomass, and their use can be implemented during daily operations of biomass fueled plants, in order to increase the sustainability of the biomass combustion process.

Acknowledgements. This research was supported by the Fondazione Cassa di Risparmio di Trento e Rovereto.

References

[1] M. O. Andreae, *Biomass Burning: Its History, Use and Distribution and its Impact on Environmental Quality and Global Climate, in Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*, MIT Press, Cambridge, Mass., 1991.

[2] I. Blanco, S. Pascuzzi, A. S. Anifantis, G. Scarascia Mugnozza, Study of a pilot photovoltaic-electrolyzer-fuel cell power system for a geothermal heat pump heated greenhouse and evaluation of the electrolyzer efficiency and operational mode, *Journal of Agricultural Engineering*, **45** (2014), no. 3, 111-118. https://doi.org/10.4081/jae.2014.238

[3] CEI-Bois, Tackle Climate Change: Use Wood. Brussels, November 2006.

[4] CEI-Bois, Memorandum to the European Institutions, Brussels, September 2009.

[5] A. Colantoni, N. Evic, R. Lord, S. Retschitzegger, A.R. Proto, F. Gallucci, D. Monarca, Characterization of biochars produced from pyrolysis of pelletized agricultural residues, *Renewable and Sustainable Energy Reviews*, **64** (2016), 187–194. https://doi.org/10.1016/j.rser.2016.06.003

[6] EN 14774-2: 2010, Solid biofuels, Determination of moisture content - Oven dry method, Part 2: Total moisture - Simplified method, CEN, European Committee for Standardization, rue de Stassart, 36 - B-1050 Bruxelles.

[7] EN 14778: 2011, Solid biofuels, Sampling. CEN, European Committee for Standardization, rue de Stassart, 36 - B-1050 Bruxelles.

[8] EN 15234:2011, Solid biofuels, Fuel quality assurance, CEN, European Committee for Standardization, rue de Stassart, 36 - B-1050 Bruxelles.

[9] EN 15297:2011. Solid biofuels, Determination of minor elements As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V and Zn, 147 Avenue Marnix 17, B-1000 Brussels, European Committee For Standardization.

[10] European Commission, 2004. Comprehensive report on the Role of Forest Products for the Mitigating of Climate Change, Directorate General Enterprise unit E.4 Forest-based industries, June 2004.

[11] European Environment Agency. EMEP CORINAIR, Emission Inventory Guidebook, Technical report, (2006).

[12] European Union, 2009, Commission Decision of 30 November 2009 2009/894/EC "On establishing the ecological criteria for the award of the Community eco-label for wooden furniture", C (2009) 9522 OJ L 320, 5.12.2009, p. 10.

[13] M. Fellin, M. Negri, Monitoring Pollutants in biomass using FT-IR-ATR technology, *19th European Biomass Conference and Exhibition*, (2011), 320 – 327.

[14] M. Fellin, M. Negri and R. Zanuttini, X-ray fluorescence as a tool for wood ecology, *Conference: ISCHP 2013 - International Scientific Conference on Hardwood Processing*, (2013), 322-326.

[15] M. Fellin, M. Negri and R. Zanuttini, Multi-elemental analysis of wood waste using Energy Dispersive X-Ray Fluorescence (ED-XRF) analyzer, *European Journal of Wood and Wood Products*, **72** (2013), no. 2, 199-211. https://doi.org/10.1007/s00107-013-0766-4

[16] M. Fellin, M. Negri, R. Zanuttini and F. Maffei, Characterization of ED-XRF technology applied to wood matrix, *Wood Research*, **59** (2013), no. 4, 533-546.

[17] M. Fellin, R. Zanuttini and M. Negri, *Monitoring Wooden Materials for Recycling*, PhD Thesis, Università di Torino, CNR-IVALSA, 2014.

[18] Finnish Standards Association, Air Quality, Stationary Source Emissions, Determination of flue gas conditions. SFS 5624, (1990).

[19] Food and Agriculture Organization of the United Nations, 2011. State of the world's forests, Rome.

[20] IPCC, 2007. Forestry in Climate Change 2007: Mitigation, *Contribution of Working Group III to the Fourth Assessment Report of the IPCC*, Cambridge University Press, Cambridge, UK & New York, USA, 2007.

[21] B.M. Jenkins, L.L. T.R. Miles Jr., T.R. Miles, Combustion properties of biomass, *Fuel Processing Technology*, **54** (1998), no. 1–3, 17-46. https://doi.org/10.1016/s0378-3820(97)00059-3

[22] L.S. Johansson, B. Leckner, L. Gustavsoon, D. Cooper, C. Tullin, A. Potter, Emission characteristics of modern and old-type residential boilers fired with wood logs and wood pellets, *Atmospheric Environment*, **38** (2004), 4183 -4195. https://doi.org/10.1016/j.atmosenv.2004.04.020

[23] Laser Mark et al., Comparative analysis of efficiency, environmental impact, and process economics for mature biomass refining scenarios, Biofuels, *Bioproducts and Biorefining*, **3** (2009), no. 2, 247-270. https://doi.org/10.1002/bbb.136

[24] P. McKendry, Energy production from biomass (part 1): overview of biomass, *Bioresource Technology*, **83** (2002), no. 1, 37-46. https://doi.org/10.1016/s0960-8524(01)00118-3

[25] P. McKendry, Energy production from biomass (part 2): conversion technologies, *Bioresource Technology*, **83** (2002), no. 1, 47-54. https://doi.org/10.1016/s0960-8524(01)00119-5

[26] P. McKendry, Energy production from biomass (part 3): gasification technologies, *Bioresource Technology*, **83** (2002), no. no. 1, 55-63. https://doi.org/10.1016/s0960-8524(01)00120-1

[27] D. Monarca, M. Cecchini, A. Colantoni, Plant for the production of chips and pellet: technical and economic aspects of a case study in the central Italy, Chapter in *Computational Science and Its Applications-ICCSA 2011*, Springer-Verlag Berlin Heidelberg, 2011. https://doi.org/10.1007/978-3-642-21898-9_26

[28] D. Monarca, M. Cecchini, A. Colantoni, A. Marucci, Feasibility of the electric energy production through gasification processes of biomass: technical and economic aspects, Chapter in *Computational Science and Its Applications - ICCSA 2011*, Springer-Verlag Berlin Heidelberg, 2011. https://doi.org/10.1007/978-3-642-21898-9_27

[29] M. Moneti, L. M. P. Delfanti, A. Marucci et al., Simulations of a plant with a fluidized bed gasifier WGS and PSA, *Contemporary Engineering Sciences*, **8** (2015), no. 31, 1461-1473. https://doi.org/10.12988/ces.2015.56191

[30] M. Negri, M. Fellin, Experimental survey with X-ray Fluorescence for multi-elemental analysis of biomasses from recovered wood, *Conference: BIT's 3rd annual World Congress of Bioenergy*, 2013.

[31] S. Pascuzzi, I. Blanco, A S. Anifantis, G. Scarascia Mugnozza, Hazards assessment and technical actions due to the production of pressured hydrogen within a pilot photovoltaic-electrolyzer-fuel cell power system for agricultural equipment, *Journal of Agricultural Engineering*, **47** (2016), no. 2, 88-93. https://doi.org/10.4081/jae.2016.507

[32] E. Pieratti, D. Antolini, P. Baggio, M. Negri, Wood combustion process: characterization of gaseous emissions of different parts of a spruce tree by means of a gasifying wood stove, *Third International Symposium on Energy from Biomass and Waste*, (2010).

[33] E. Pieratti, D. Antolini, A. Boschetti, P. Baggio, M. Scotoni, Gaseous Emissions and Volatile Organic Compound Characterization from a Gasfying Wood Stove for Residential Application, *19th European Biomass Conference and Exhibition*, (2011).

[34] Andrea R. Proto, Giuseppe Zimbalatti, Lorenzo Abenavoli, Bruno Bernardi, Soraya Benalia, Biomass Production in Agroforestry Systems: V.E.Ri.For Project, *Advanced Engineering Forum*, **11** (2014), 58–63. https://doi.org/10.4028/www.scientific.net/aef.11.58

[35] G. Russo, A. S. Anifantis, G. Verdiani, G. Scarascia Mugnozza, Environmental analysis of geothermal heat pump and LPG greenhouse heating systems, *Biosystems Engineering*, **127** (2014), 11-23. https://doi.org/10.1016/j.biosystemseng.2014.08.002

[36] E. Smidt, K. Meissl, M. Schwanninger, P. Lechner, Classification of waste materials using Fourier transform infrared spectroscopy and soft independent modeling of class analogy, *Waste Management*, **28** (2008), 1699–1710. https://doi.org/10.1016/j.wasman.2007.08.003

[37] E. Smidt, K. Meissl, The applicability of Fourier transform infrared (FT-IR) spectroscopy in waste management, *Waste Management*, **27** (2007), 268–276. https://doi.org/10.1016/j.wasman.2006.01.016

[38] Ilaria Zambon, Fabrizio Colosimo, Danilo Monarca, Massimo Cecchini, Francesco Gallucci, Andrea Proto, Richard Lord, Andrea Colantoni, An Innova-

tive Agro-Forestry Supply Chain for Residual Biomass: Physicochemical Characterisation of Biochar from Olive and Hazelnut Pellets, *Energies*, **9** (2016), no. 7, 526. https://doi.org/10.3390/en9070526

Received: August 1, 2016; Published: November 18, 2016