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ORIGINAL PAPER

Quantitative and Qualitative Analysis of Biomass from Agro-industrial Processes in the Central Macedonia Region, Greece

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Abstract This work aims to identify the potential biomass resources produced in the area of the Central Macedonia Region, in Northern Greece, in order to contribute to the efforts to achieve national targets for renewable energy sources. Specific objectives included the evaluation of the biomass amounts in each regional unit, the measurement of their characteristics and properties, and the investigation of their utilization potential. According to this survey, a total of 1.33 million tonnes of fresh biomass residues are produced in the Greek Central Macedonia Region. The utilization potential of available biomass resources may be evaluated according to the quality characteristics of the various types of biomass based on the results of laboratory tests and classified in the following ranking in descending order: peach and olive stone, cotton residues, almond shell, olive cake, pressed grape skins, peach pulp and peach and potato peels. The residues from oil production and cotton mill residues are of high importance. Agricultural residues remaining in the farming areas, such as olive and peach branches, represent another challenging biomass source. Furthermore, according to the survey for each regional unit, there is a significant number of biomass types that could be utilized, after appropriate management. An efficient management plan should be based on the use of biomass resources with a regular production regime over the year, such as manure or potato residues, combined with or supported by the sequential use of various other residues produced through the year, on a temporary basis. Thus the presence of different types of biomass resources in the specific area, with seasonal variability, could justify the continuous availability of raw materials all year round.

Keywords Agro-industrial units · Biomass potential · Biomass quality properties · Renewable energy sources · Bio-energy · Central Macedonia Region

Introduction

In June 2010, the Greek Parliament adopted new legislation, Law 3851/2010, related to renewable energy production. According to this legal document, the cost of electricity produced from biomass and sold to the power grid was increased overnight by more than 150 %. The price of each MWh of electricity produced from biogas or syngas could reach up to 250 €/MWh, while a reduced price of up to 230 €/MWh has been established when electricity is produced by conventional combustion processes. Nevertheless, it should be stressed that these prices represent high values for renewable energy, being the second highest in the EU countries [1].

In 2012, as part of the efforts to reduce public debt, the tax on diesel used for heating was raised to the same prices as that used for transport. Diesel is the most commonly

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used heating fuel in Greek households. That measure resulted in a 68.7 % reduction of the diesel volumes used, from 1,833,800 tn in the winter of 2011–2012 (October–February) to 567,634 tn in 2012–2013 (October–February) [2]. However, the adoption of this measure had an important side-effect: a dramatic shift of the local heating market to alternative fuels was observed, mainly towards wood pellets. A 25 % increase was noted in the boiler market in Northern Greece alone, mainly in the suburbs of Thessaloniki, capital of the Central Macedonia Region and the second largest city in Greece (with a population of over 800,000 [3]).

Over the following years, these measures completely changed the approach towards biomass utilization in the country. Biomass had hitherto usually been disposed of in an uncontrolled way, often by incineration in small scale incinerators, resulting in significant environmental impacts. However, as soon as these measures were adopted, biomass was no longer considered as waste to be disposed of, but a valuable alternative fuel. To date, more than 1400 applications have been submitted for the installation of biomass energy production units [4]. The quota of 400 MWe power to be installed by 2020 has been exceeded by a factor of at least five. Moreover, over ten pellet-producing units have been installed in Greece, with a total production capacity exceeding 100,000 tonnes of pellets per year.

However, after 3 years, only ten biomass energy utilisation units have been constructed while the pellets produced by Greek companies never exceeded 10,000 tonnes per year. This could be attributed to several factors, such as the overall Greek economic environment, and the absence of bank support for any investment. In addition, although a high biomass utilization rate is expected, an extended inventory of potential available biomass resources is missing; such an inventory should include information about the whole chain of the biomass management process, such as production, availability, collection system and transportation of the biomass produced in fields and agro-industrial units, and the possibility of transforming it into usable fuel. There is a similar lack of information and adequate data in a large number of countries, especially in the Mediterranean region, representing the single largest obstacle to the viable energy utilisation of biomass. Nevertheless, the wood pellet market is booming in Europe [5]: approximately 650 pellet plants produced more than 10 million tonnes of pellets in 2009 in Europe. Total European consumption was about 9.8 million tonnes, of which some 9.2 million tonnes is within the EU-27, representing a modest 0.2 % of gross energy consumption (75 EJ level in 2008).

A number of studies have been presented in the literature concerning this subject worldwide. In recent years, about 110,000 tn wood pellets and briquettes (80 % of those produced) and about 68,000 tn of biodiesel have been exported annually from the Czech Republic to other EU countries [6, 7]. Biomass is the major source of energy in rural Turkey. The total biomass energy potential of Turkey is about 32 Mtoe. The amount of usable biomass potential of Turkey is approximately 17 Mtoe. The electrical production from usable biomass has a net impact of $4.4 billion in personal and corporate income and represents more than 160,000 jobs [8]. According to Fernandes and Costa [9], in one region of Portugal (Marvão) the annual biomass residue potential is about 10,600 tonnes, which corresponds to an energy production potential of about 106,000 GJ per annum. Finally, the amount of agricultural and forest residues available for bioenergy in Romania was estimated at 228.1 PJ on average, of which 137.1 PJ was from annual crop residues, 17.3 PJ from permanent crop residues and 73.7 PJ/year from forestry residues, firewood and wood processing by-products. The biomass availability shows large annual and spatial variations, between 135.6 and 320.0 PJ, due to the variation in crop production and forestry operations [10]. One of the most important steps in developing biomass energy supply from residues is to evaluate their spatial and temporal availability. Such an analysis would provide useful information for decision makers on the opportunities for using biomass residues for energy applications in the country.

This paper presents the results of an extensive survey in the Central Macedonia Region that took place in the period 2011–2012, aiming to monitor and qualitatively and quantitatively analyse the available biomass resources produced by the agro-industrial units located in this particular region. Such an inventory aims to support the decision-making process for the biomass utilization potential based on the availability of the resources produced in the specific region, and could be extended to other rural areas, especially in the Mediterranean region. The specific area has received a great deal of investment interest, due to excess availability of various types of biomass (agricultural and forest biomass, forage and agro waste, etc.), as evidenced by the large number of applications submitted over the past 2 years. Specifically, the total installed capacity requested reaches up to 91.67 MW, of which only 8 MW refer to existing power stations already in operation.

Materials and Methods

The quantitative and qualitative analysis of biomass in the Greek Central Macedonia Region was carried out through two subsequent operational stages, according to the following:

1. Identification of potential biomass resources,
2. Evaluation of the compositional characteristics of the various types of biomass.

Identification of Potential Biomass Resources

During the first phase of the survey, efforts focused on determining the primary biomass resources in the Central Macedonia Region, in order to identify their potential availability.

The region of Central Macedonia is located in Northern Greece and consists of the following Regional Units (RU): RU Imathia, RU Thessaloniki, RU Kilkis, RU Pella, RU Pieria, RU Serres and RU Chalkidiki.

For each RU, the collected information related to biomass production included:

- Existing agro-industrial plants producing crop residues; each plant was classified according to the corresponding activity,
- Quantities and types of residues per plant,
- Crop cultivation lands and the corresponding production rate per region.

A total of 23.650 tn cotton mill residues were recorded and 14 samples were collected. 22.800 tn and 28 samples were recorded and collected from olive oil mills, 15.066 tn and 11 samples from Canning and Juice Units, 4.850 tn and 9 samples from Rice and Almond Mills, and 356 tn and 9 samples from Wineries.

The residues considered in this work were generated from agricultural crop production (rice, wheat, maize, cotton, and sugar beet) and pruning of vineyards and orchards (olive, peach, apple and cherry). The assessment of the agricultural crop residue availability included several site-specific factors such as crop yields, multi-annual yield variation, environmental constraints and competitive uses. The estimate of agricultural residues is based on specific total residue to product ratios, depending on crop type and yield. The estimates of pruning residues from fruit tree plantations and vineyards are based on current orchard and vineyard areas and specific residue ratios.

As a result of varying local conditions, the estimates of the amount of residues vary widely and have a high degree of uncertainty. Several studies proposed different values for sustainable removal rates of crop residues. The crop residue yields vary even more than the crop yields [11, 12] and are therefore difficult to account for, as they depend on plant variety, location, climate conditions, farming practices and other factors [13, 14]. The values for residue to yield ratios, dependent on crop types, were obtained from a literature survey, as well as field visits and discussions with growers and agronomists. Frequently, in different studies, a constant crop to residue production ratio is assumed [15–17], which might not be valid as the ratio varies greatly across different sites/climates, plant types, farming practices, annual yields, etc.

The residues generated from the pruning of orchards (apples, pears, plums, peaches, apricots and cherry trees) consist of small branches and biomass resulting from regular and cleaning operations. Little information is available on pruning residues. However, several studies propose some figures for the ratios of residue to product yields for pruning [18–21]. These data show a certain scattering and must be used with caution. The available data were compiled and conservative data were used in the computation of the available biomass from pruning. In most cases there was a general ignorance, and estimates presented are based on population and average, for Northern Greece, estimated a pruning production per capita of up to 3.0 kg/year.

The information required for the inventory was collected using several approach methods, i.e. personal communication, emails or faxes sent to official administrative personnel in Services, Agencies and Chambers of the respective regions. Information was collected from data available on websites or through direct visits to the producers or plants. An appropriate questionnaire was developed in order to enhance the process. The specific institutions contacted for data collection are presented below:

The various departments of the regional authority of Central Macedonia, including the following: Department of Licensing Development, Energy and Natural Resources, Department of Agricultural Development, Directorate of Agriculture and Veterinary Medicine, Department of Industry, Energy and Natural Resources RCM. General Directorate of Rural Economy and Regional Veterinary Medicine—Department of Quality and Phytosanitary Control, Chamber of Commerce and Industry (http://www.imathiachamber.gr, https://echamber.ccikilkis.gr, http://www.pellachamber.gr, http://www.serreschamber.gr), Greek Yellow Pages (http://www.xo.gr).

During the site visits, a questionnaire was completed, including additional available data and comments on residual products, such as hardware, origins, smell creation, storage, use or disposal methods, etc.

After the preliminary investigation of potential biomass resources, a sample collection campaign was designed, for the collection and characterization of various biomass types. Special efforts were made to collect as many available biomass resources as possible, reflecting spatial and temporal (seasonal) variability.

The approach plan applied during the collection campaign included:

- Initial communication with those in charge of the production plants;
- On-site visit and completion of the questionnaire;
- Sampling according to Standard method EN CEN/TS 15442 [22];
- Transport of samples to the laboratory and analysis to determine their characteristic properties.

Sample Collection

Sample collection took place according to the ELOT CEN/TS 15442 standard method. 150 samples of different biomass types were collected in total. The sampling process was defined considering the general characteristics of the sample (accessibility, quantity, shape, geometry, sampling equipment).

According to the standard method, sampling was carried out in a static mass pile of materials and a minimum of 24 sampling positions were selected. The minimum size of each of the 24 sampling positions making up the final sample volume was determined by the following equations:

$$m_m = 2.7 \times 10^{-8} \times d_{95}^3 \times \lambda_s, \quad \text{if } d_{95} > 3\,\text{mm} \tag{1}$$

and

$$m_m = 1.0 \times 10^{-6} \times \lambda_s, \quad \text{if } d_{95} < 3\,\text{mm} \tag{2}$$

where m_m: mass of the minimum size of each position in kg, d_{95}: nominal maximum grain size of the material in kg/m^3, λ_s: flux density of the mass in kg/m^3.

Sample collection took place from August 2012 to December 2012; the extended sampling period was required in order to collect as many sources of biomass as possible, taking into account that the production regime varied significantly depending on the particular season time.

Analysis of Biomass Sample Properties

The collected samples were stored in airtight plastic bags or containers, placed in a dark room and analyzed to determine their moisture content, heating value, and fixed carbon, volatile and ash content, using standard analysis methods [23, 24]. Finally, the samples were stored in a dry place, while for samples with moisture content >15 %, analysis of their moisture content took place before the performance of the other relevant tests.

Specifically, the following analysis methods were used: Moisture (CEN/TS 15414/02: 2006) [25], pH (using Crison pH-meter, GLP 21), Higher Heating Value, HHV (CEN/TS 15400) [26], Lower Heating Value, LHV (CEN/TS 15400), Volatile matter (CEN/TS 15402) [27], Sulfur (S) and Chlorine (Cl) (CEN/TS 15408) [28] and Ash (CEN/TS 15403) [29].

According to the CEN/TS 15414/02: 2006 methodology, the moisture content of each sample was determined by drying. A small amount of sample was weighed, placed in a capsule and introduced into the furnace (WTW CR 3000) at a temperature of 105 °C. By measuring the weight loss of the sample before and after heating, moisture content was calculated. Regarding pH, aqueous solutions were formed based on the moisture content of each sample, and the solution pH was measured with a Hanna Instruments HI 9023 CN pH meter.

Determination of the energy content of solid samples carried out by the CEN/TS 15400 methodology. One gram of sample is introduced into an oxygen chamber, compressed in an oxygen atmosphere (30 bar) and then immersed in a tank of water. The increase in water temperature during the combustion of solid in the chamber results in the calculation of gross calorific value of the sample.

After combustion the chamber is rinsed with distilled water and the collected rinsing liquid is used to calculate the concentration of sulfur and chlorine in the samples, as described in standard test CEN/TS 15408:

- Determination of sulfur by the barium sulphate $BaSO_4$ gravimetric method, in which barium sulfate precipitation occurs, and by measuring the content of the residue using a turbidimeter, and
- Determination of chlorine by the Mohr/Volhard method, in which precipitation occurs in chlorides in the presence of chromate ions, which act as receptors.

Volatile content was measured in a similar manner to moisture using the CEN/TS 15402 method. The sample was placed into the oven at 900 °C for 7 min.

The CEN/TS 15403 method was used to determine the ash content: a quantity of sample is introduced into the furnace with the temperature switched according to a profile ranging from 100 to 550 °C at different intervals. The temperature profile applied to the pre-dried samples included increasing the temperature up to 250 °C, standing for 1 h, heating to 550 °C and standing for 2 h.

Results and Discussion

The aim of this work was the identification of the potential available biomass resources in the Region of Central Macedonia in Northern Greece (Fig. 1), produced from agricultural and industrial activities; towards this purpose efforts were paid to determine the production rates of agricultural residues, taking into account their spatial and

Fig. 1 Central Macedonia Region, Greece map

temporal variation and their corresponding properties, for their utilization.

The amounts of various agricultural residues were estimated for the Central Macedonia Region, including the following biomass types:

- Biomass from agricultural plants,
- Biomass residues remaining in the field after the completion of crop activities

Data were collected for various agro-industrial facilities such as cotton mills, olive oil mills, canning and juice units, rice and almond mills and wineries.

Current Solid Residue Management Practices in Agro-industrial Activities of the Target Area

Cotton mills (CM) usually operate from October to December and their end product is cotton. The cotton residues (CR) are called “mixed” or “junk” wastes, containing plant residues, dust and various types of fibers, and are freely available to farmers. A significant number of plants have started or intend to utilize these residues as an alternative fuel to replace oil or natural gas. The replacement ratio, based on their energy content and given a typical HHV value of about 16.4 MJ/kg [30], is around 10–12 tonnes residues to 1 tonne oil at a price of €85–100. However, only a low utilization rate of these biowastes is currently observed, attributed mainly to the investment costs required to build up a biomass energy utilization system. CRs are currently utilized on-site for soil amendment, in combination with the cotton crop residues. It is estimated that around 5–7.5 tonnes of plant stalks remain per each acre, currently incorporated plowed back into the field to enrich the soil. This quantity is gathered by reapers, and the associated cost per acre is estimated at about €50–100.

Several researchers have examined the energy utilization of cotton mill residues: Zabaniotou et al. [31, 32] examined the feasibility of energy production from cotton ginning and other agricultural residues in a pilot scale system, especially for countries with rough topography based on agricultural activities. Petrou and Mihiotis [33] proved that the substitution of cotton stalks for conventional fuel in the industrial sector is both technically and economically feasible. Moreover, Akdeniz et al. [34] stated that the establishment of a well-organized biomass (cotton residue) management policy would be helpful for the optimum utilization of agricultural residues in the energy production sector.

Olive oil mills (OM) usually operate from October to December and their end product is olive oil. Olive cake (OC) and olive stone (OS) are the main residues of OM. From the mass balance of a 3 phase olive oil mill, it is deduced that 1 kg of olives and 2.65 kg of water produce about 0.21 kg olive oil, 0.09 kg olive leaves, 0.35 kg olive cake and 3 kg olive mill waste water at the system outlet. OC, according to the present availability survey of management olive plants, is freely available at olive cake factories and 10 % of olive pits are returned for burning. Based on the data presented, it should be particularly stressed that OM residue disposal/management in Northern Greece is very well-developed. This implies a relatively low selling price, which is not going to remain at these levels; prices will certainly increase, as OC makes an excellent fuel after moisture reduction (Table 3). Finally, olive tree branches amount to 8–10 kg per tree. In conclusion, the difficulty in residue collection and processing (crushing and drying) results in a high utilization cost, representing the main barrier to their exploitation.

Canning and Juice Units (CJ) operate between July and September and their end product is peach. The peach crop provides a number of residues both in the field (branches) and during the manufacturing process that absorbs the majority of production, either canning or juice production. Three main residues are produced during the manufacturing process: peach core (PC), peach peel (PEPE) and peach pulp (PEPU) produced by the biological wastewater treatment plant. The PC is available free to greenhouses for heating or sold at prices from 30 to 70 €/tn. PEPE is given free as fertilizer to stock farms or is returned to juice processing. The pulp from the biological system has a treatment cost of about 40–80 €/tn. Finally, the requirements for potential alternative uses of CJ by-products include the removal of the remaining flesh from peach cores and their use as fuel for the operation of the plant.

Rice (RM) and almond mills (AM) operate from September to November and /or September to December; their end product is rice and almond respectively. Rice husk has several applications in poultry farms, while it can be used in lime-cement industries for use as an alternative fuel. The almond shell (AS) is exploited as a domestic heating fuel sold for about 15 €/tonne. Nevertheless, an alternative utilization of this residue is not apparent.

Winery (W) residues are produced from September to November. Winery residues consist of pressed grape skins (PGS) which are generated during wine production by industrial wineries, and residues produced in smaller amounts at the vineyard. Usually, PGS are further used to produce a local spirit; they are also applied as a soil amendment without further processing or stockpiled for approximately 1 year for composting [35].

In addition to the above residues, there are other agricultural and agro-industrial activities producing significant amounts of good quality biomass (with high Higher Heating Value and low ash and moisture content). The main activities and the corresponding residues include:

- Poultry and sheep farms producing manure. Manure is produced throughout the year, with a selling price of around 10 €/tn, and is available almost exclusively to farmers.
- The strain of rice crops which is not used as animal feed but is usually burned in the field.
- Straw is about 50 % by weight of wheat and is baled and sold mainly to farmers or burned in the field.
- Apple, peach and cherry branches amount to 8–10 kg per tree and are usually burned in the field or converted to pellets.
- Potato processing residues are produced throughout the year. In addition, potato peel (POPE) is provided to the market without any cost and is usually freely available to farmers.

Production of Residues from Agro-industrial Activities in the Region of Central Macedonia

Data related to total cultivation surfaces, production rates and quantities of residues in the area of Central Macedonia are presented in Table 1.

In the Imathia Region, more than 40,000 tonnes of fresh agro-residues from 16 units were accounted for, and more than 250,000 tn fresh residues of five main crops: rice, wheat, maize, cotton and peach. Therefore the Imathia Region seems to produce over 300,000 tonnes of biomass that could be utilized for energy production. In the Thessaloniki Region more than 5000 tonnes of agro-residues from 6 units were estimated, and more than 250,000 tonnes of residues of five main crops: rice, wheat, maize, cotton and olive. Thus over 250,000 tonnes of biomass are available in the area of Thessaloniki. In the Pella Region more than 13,000 tonnes of agro-residues from 10 units were estimated and more than 90,000 tonnes of residues of four main crops: peach, olive, cherry and apple. Therefore the Pella Region seems to produce more than 100,000 tonnes of biomass that could be utilized for energy production. In the Pieria Region more than 4000 tonnes of agro-residues from 6 units were estimated and more than 100,000 tonnes of residues of five main crops: wheat, maize, cotton, sugar beet and olive. Thus the Pieria Region seems to produce over 105,000 tonnes of biomass. In the Serres Region more than 16,000 tonnes of agro-residues from 36 units were accounted for, and more than 390,000 tonnes of residues of four main crops: rice, wheat, maize, cotton, and olive. Therefore the Serres Region

Table 1 Quantitative estimate of biomass produced in the field in prefectures of the region

Region	Cultivation activities	Cultivation surfaces (acres)	Production (tn)	Quantities of residues in the field (tn) per year	Fresh residues from agroindustrial units (tn)
Imathia	Rice	1950	15,600	7500	16 units
	Wheat	5800	17,000	8000	
	Maize	6000	60,000	40,000	
	Cotton	15,500	40,000	124,000	
	Peach	19,000	300,000	76,000	
	Total	48,250	432,600	256,000	40,000
Thessaloniki	Rice	20,000	160,000	80,000	6 units
	Wheat	30,000	90,000	45,000	
	Maize	5,500	55,000	44,000	
	Cotton	8000	20,000	64,000	
	Olive	5000	12,500	15,000	
	Total	68,500	337,000	248,000	5,000
Kilkis	Grape	600	5500	1800	150
Pella	Peach	16,600	292,000	66,000	10 units
	Olive	735	2500	2200	
	Cherry	7100	16,900	21,000	
	Apple	1880	49,000	7500	
	Total	26,315	360,400	96,700	13,000
Pieria	Wheat	20,000	60,000	30,000	6 units
	Maize	2000	20,000	16,000	
	Cotton	4600	14,000	45,000	
	Sugar Beet	690	38,000	15,000	
	Olive	3330	1000	900	
	Total	30,620	133,000	106,900	4500
Serres	Rice	5000	25,000	12,500	36 units
	Wheat	66,000	190,000	95,000	
	Maize	17,500	220,000	122,000	
	Cotton	17,800	50,000	140,000	
	Olive	5500	14,000	22,000	
	Total	111,800	499,000	391,500	16,000
Chalkidiki	Wheat	32,000	100,000	50,000	28 units
	Olive	31,000	100,000	95,000	
	Total	63,000	200,000	145,000	10,000

seems to produce over 400,000 tonnes of biomass that could be utilized for energy production. Finally, in the Chalkidiki Region more than 10,000 tonnes of agro-residues from 28 units were estimated, and more than 140,000 tonnes of fresh residues of two main crops: wheat and olive. Thus the Chalkidiki Region seems to produce more than 150,000 tonnes of biomass. Skoulou et al. [36] reported about 4000 kg/ha of energy crop residues in Greece.

According to Fernandes and Costa [9], the estimated agriculture residue potential in a region of Portugal (Marvão), is about 7973 tn/year. Residue production is mainly based on cereal cultivation and olive yard residues, which total 6950 tn/year.

The seasonal variation of the examined residues is given in Fig. 2. Quantitative variation (cumulatively for each kind of residue) of different residues is shown, following the corresponding production period. It is obvious that most agro-residues are produced between July and November, while more than 70,000 tn residues of the total 92,000 tn are produced from September to November. It is worth noting that only manure is produced throughout the year.

One of the most important characteristics of biomass, critical to the development of an appropriate utilization policy, is its availability during the year. Following the agricultural production regime of each material, the corresponding residues are produced in certain time periods;

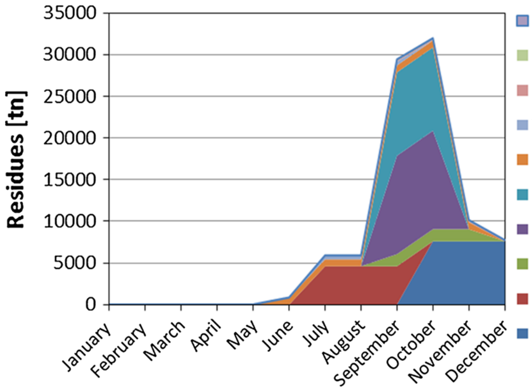

Fig. 2 Quantitative depiction of the temporal variation of agro-residue production

however, continuous energy is required over the course of the year. The storage of biomass for long periods creates heavy demand for storage area associated with a high cost. Therefore an efficient management plan should be based on the use of biomass resources with a regular production regime over the year, such as manure or potato residues, and the sequential use of various residues produced during the year. The cumulative biomass production in each regional unit is given in Table 2, accounting for residues produced and remaining in the fields and residuals from the processing of raw materials in the corresponding agro-industrial units. As shown in this table, the latter residues amount to about 7 % of the total biomass potential, the greater part corresponding to the residuals remaining in the field.

Agricultural waste such as cotton straw, rice husk, dry olive kernels, corn and soya residues, as well as walnuts and kernels, comprise an alternative energy source. Significant quantities of these biomass types can be utilized to produce sufficient thermal power to meet the energy needs of small to medium size industrial units as well as for distant heating of buildings [32]. The available energy potential derived from agricultural biomass species for the Central Macedonia Region corresponds to 313,779 tonnes of cotton mills and cotton shanks, 89,000 tonnes of rice residues, 152,460 tonnes of peach tree branches, 29,400 tonnes of peach cores and 318,000 tonnes of olive tree branches. The available biomass energy potential is enough to cover 10 % of national annual heating oil consumption. However, the cost associated with the energy utilization of biomass can be quite high, due to the high cost of transportation and logistics [32].

Energy Utilization and Characteristic Properties of Agro-industrial Residues in the Target Area

Biomass energy conversion technologies cover a wide scientific and technological range, and the applicability of each method relies on the particular biomass fuel, as well as on the desired end product. In general, such methods include thermochemical processes (combustion, gasification, pyrolysis), suitable for biomass species with low moisture content and high carbon fraction, and biochemical processes (aerobic and anaerobic fermentation), which are suitable for biomass species with high moisture content [32].The end product of each biomass utilization process could be thermal energy for industrial applications, which is the most common option, as well as electricity production and co-generation of heat and electricity in distributed consumption systems. Nevertheless, thermal processing of organic waste materials can result in heat production or the formation of a number of liquid or gaseous fuels [32].

In order to investigate the energy utilization potential of available biomass resources in the target area, 58 samples of various biomass types were analyzed for the determination of their characteristic properties.

Minimum, maximum, mean and standard deviation values of the corresponding physicochemical parameters are given in Table 3. The mean values of heating values and ash and volatiles content for the various biomass samples are shown in Figs. 3 and 4 respectively.

The analysis of the physicochemical parameters of pressed grape skins, olive cake, peach pulp and peel, and potato and onion peel showed that all biomass resources presented high moisture content associated with a reduction of combustion temperature during thermal treatment. PGS mean value of moisture content was found to be 60.8 ± 11.1 %, OC 58.8 ± 5.7 %, PEPU 78.1 ± 11.2 %, PEPE 88.1 ± 1.6 %, POPE 84.7 ± 4.2 % and onion peel 74 %.

Table 2 Quantities of biomass recorded in the Central Macedonia Region of Greece

Source residues	Region Unit						
	Imathia	Thessaloniki	Kilkis	Pella	Pieria	Serres	Chalkidiki
Agro-industrial units (tn)	40,000	5,000	150	13,000	4500	16,000	10,000
Quantities of residues in the field (tn)	256,000	248,000	1800	96,700	106,900	391,500	145,000
Total	296,000	253,000	1950	109,700	111,400	407,500	155,300

Table 3 Qualitative analysis of samples

Biomass type	Value	Moisture (%) (a.r.)[a]	Ash (%) (d.m.)[b]	Volatiles (%) (d.m.)	pH	HHV (kcal/kg) (d.m.)	LHV (kcal/kg) (b.r.)[c]	Cl (%)	S (ppm)
Pressed grape skins	Min	47.3	8.6	73.4	4.8	4737.3	1258.2	0.03	34.4
	Max	73.6	15.0	85.7	5.0	4931.8	2600.0	0.03	111.3
	Mean	60.8	11.3	80.5	4.9	4828.9	1860.2	0.03	77.4
	SD	11.1	2.9	5.1	0.1	93.9	560.2	0.00	31.9
Cotton residues	Min	8.3	9.6	80.8	5.8	3696.8	1789.3	0.04	53.3
	Max	57.2	25.6	91.2	6.5	4179.7	3720.2	0.05	170.7
	Mean	16.7	16.7	86.6	6.1	3943.3	3274.6	0.05	114.9
	SD	15.5	4.6	3.2	0.2	149.4	576.2	0.00	31.1
Olive cake	Min	50.9	1.2	89.6	5.0	4252.7	1530.6	0.03	7.6
	Max	70.3	5.8	96.6	5.8	5732.4	2407.3	0.05	120.4
	Mean	58.8	2.5	93.6	5.4	4900.0	2013.8	0.04	37.7
	SD	5.7	1.1	1.7	0.2	430.9	296.7	0.01	35.7
Olive stone	Min	42.9	1.7	93.0	5.1	4713.5	2453.8	0.04	20.0
	Max	48.9	2.5	93.4	5.4	4758.1	2757.6	0.05	75.0
	Mean	44.8	2.0	93.2	5.3	4735.0	2642.1	0.04	60.0
	SD	2.8	0.4	0.2	0.1	21.7	132.2	0.01	26.7
Peach core	Min	16.1	0.2	95.5	5.3	4713.7	2861.1	0.04	1.0
	Max	42.0	0.8	98.5	5.7	5251.9	4026.6	0.04	6.0
	Mean	29.1	0.4	96.8	5.6	4961.8	3431.7	0.04	3.6
	SD	10.9	0.2	1.2	0.2	210.1	525.7	0.00	2.1
Peach pulp	Min	63.0	1.8	75.6	4.1	43,251	417.4	0.03	6.0
	Max	90.9	35.0	86.0	7.7	5563.0	1707.5	0.05	168.0
	mean	78.1	15.9	80.8	6.7	4810.3	978.3	0.04	49.3
	SD	11.2	14.8	4.1	1.3	505.1	474.8	0.01	68.0
Peach peel	Min	86.7	9.3	80.1	3.6	4300.6	483.9	0.03	19.0
	Max	89.9	14.5	89.8	4.4	4786.7	572.0	0.03	84.0
	Mean	88.1	11.7	86.4	4.1	4551.3	538.1	0.03	53.0
	SD	1.6	2.6	5.5	0.5	243.4	47.4	0.00	32.6
Potato peel	Min	81.1	5.0	81.1	5.7	3912.9	431.5	0.04	21.0
	Max	89.2	7.3	95.5	6.4	4010.1	753.7	0.05	40.0
	Mean	84.7	6.1	90.5	6.0	3969.6	607.8	0.05	28.3
	SD	4.2	1.2	8.2	0.4	50.6	163.2	0.01	10.2
Almond shell	Min	9.8	2.6	89.4	5.2	4618.3	4111.6	0.03	2.0
	Max	10.1	3.0	91.8	5.2	4688.7	4213.8	0.04	4.0
	Mean	10.0	2.8	90.6	5.2	4653.5	4162.7	0.03	3.0
	SD	0.2	0.2	1.7	0.0	49.8	72.2	0.00	1.4
Onion peel		74.0	1.8	96.3	5.4	3331.3	866.1	0.06	27
Bran		11.5	3.0	84.9	5.9	4228.7	3742.8	0.04	32
Seed corn		13.1	4.6	90.2	5.7	4325.3	3760.8	0.04	49
Rice shell		8.4	19.6	94.5	4.3	3622.2	3316.9	0.04	89
Olive core (elaborated)		12.9	1.9	91.5	5.4	5247.2	4570.8	0.03	23
Hen manure		25.6	44.0	88.2	7.9	2310.3	1718.9	0.11	102
Sheep manure		43.4	23.2	88.1	7.6	3865.0	2188.0	0.06	84

[a] a.r. means as received, parameter analyzed in the samples as received by the analyst

[b] d.m. means dry matter, value expressed on dry basis

[c] b.r. means by reduction of HHV

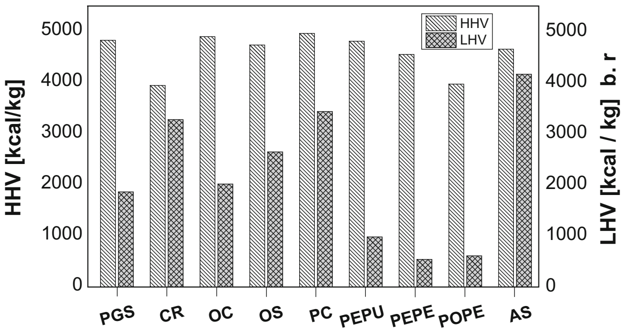

Fig. 3 Mean HHV και LHV of the various types of biomass per dry basis; *PGS* pressed grape skins, *CR* cotton residues, *OC* olive cake, *OS* olive stone, *PC* peach core, *PEPU* peach pulp, *PEPE* peach peel, *POPE* potato peel, *AS* almond shell

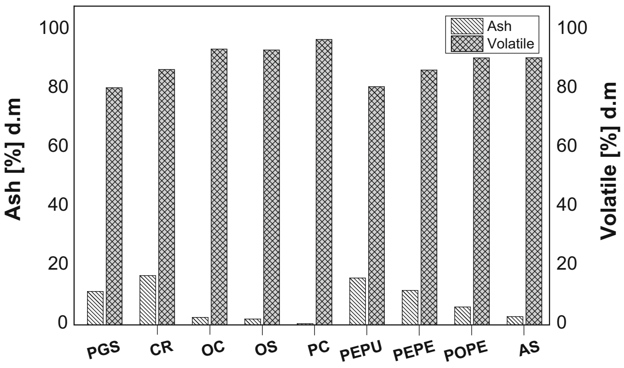

Fig. 4 Mean ash and volatiles of the various types of biomass per dry basis; *PGS* pressed grape skins, *CR* cotton residues, *OC* olive cake, *OS* olive stone, *PC* peach core, *PEPU* peach pulp, *PEPE* peach peel, *POPE* potato peel, *AS* almond shell

The variation of energy content (HHV and LHV) of nine different types of biomass is shown in Fig. 3. These values are expressed on a dry basis. The Higher Heating Value of the biomass samples varied from 3943 to 4962 kcal/kg. As shown in Fig. 3, the highest HHV values were observed for peach, olive stone, and olive cake, while the lowest HHV values were measured for cotton residues. However, the highest values of LHV were found for almond shell, reaching to 4160 ± 72 kcal/kg, while samples of peach and potato peel have the lowest values, 540 ± 47 kcal/kg and 610 ± 160 kcal/kg respectively. The different moisture content affects HHV values. The higher the moisture content, the lower the HHV value [37]. HHV is the total energy content released when the fuel is burnt in air, including the latent heat contained in the water vapor, and therefore represents the maximum amount of energy potentially recoverable from a given biomass source [23]. Heating value decreases with moisture content, so excessive moisture levels can reduce combustion temperatures, affecting the efficiency of the process [38].

The variation of ash and volatile content of biomass samples is given in Fig. 3. The highest ash value was obtained for peach pulp (15.9 ± 14.8 %) and cotton residues (16.7 ± 4.6 %) while the lowest values were measured for peach core (0.4 ± 0.2 %) and olive stone (2.0 ± 0.4 %). Energy available from the fuel is reduced linearly by the ash content [23]. In a thermo-chemical conversion process, the chemical composition of the ash can result in significant operational problems. This is especially true for combustion processes, where the ash can react to form ‘slag’, i.e. a liquid phase formed at elevated temperatures, which can reduce plant throughput and results in increased operating costs [23].

However, more constant values were observed in the volatile content; volatiles ranged from 80 ± 5 % in pressed grape skins to 97 ± 1.2 % in peach stones without fluctuations in different biomass types. Volatile content is important during energy utilization as it provides a measure of the ease with which the biomass can be ignited and subsequently gasified, or oxidized, depending on the method applied for the energy utilization of the biomass [23]. Biomass generally has a very high volatile content, with typical values of about 75 %, although increased values reaching up to 90 % have been measured, depending on the sample [39].

Chlorine content was generally low in all samples, ranging from 0.03 to 0.05 %, while sulfur content varied from 3 (almond shell) to 115 ppm (cotton residues). The presence of chlorine and sulfur is important, due to the potential formation of toxic compounds in the flue gases, while their combination with K may result in corrosion problems [40].

Utilization of Various Agro-industrial Residues as Energy Sources

Agricultural residues represent a significant energy source in an area that could contribute to the development of a self-sustaining energy policy and favor the production of lower amounts of disposable waste. However, an appropriate plan for the energy utilization of agro-industrial residues in an area should take into account the primary physicochemical properties of each available stream of residues, compared to other potential energy sources.

Pressed Grape Skins

As shown in Table 3, the higher heating value of pressed grape skins varied from 4737.3 to 4931.79 (kcal/kg) on dry matter, slightly higher than typical HHV for grape skins in the Phyllis Database [30] which range from 18.6 to 19.8 MJ/kg (4442 to 4729 kcal/kg). The characteristic properties of PGS are the low amount of ash, the high content of volatiles, over 80 %, and the significant moisture content. Typical values of grape skin ash content vary from 4.2 to 9.5 % [30, 41, 42] and volatile matter from 66.1 to 68.3 % [30, 43].

Comparing the results of this study with the published data, higher ash content was observed with a mean value of 11.3 ± 2.9 % and high volatiles. Currently, pressed grape skins are generally mixed with other biomass sources of higher quality, like wood chips, to improve energy content and reduce ash content [40].

Cotton Residues

The mean HHV of cotton residues is reported at about 3943 ± 149 kcal/kg or 16.5 MJ/kg on dry matter, while low moisture content was measured in the examined samples, which however represented the highest ash content of all examined biomass types. Typical ash values in the Phyllis Database [30] range from 14.8 to 17.6 % while the HHV is 16.4 MJ/kg. Therefore, cotton residues may become an interesting source for further use without any additional processing, due to low moisture content. However, the high ash content and soil in the residues may represent a significant barrier to further utilization.

Olive Residues

HHV of olive cake ranged from 4252.7 to 5732.4 kcal/kg while the HHV of olive stone varied from 4713.5 to 4758.1 kcal/kg, which are similar to the reported values in the Phyllis Database [30]: olive cake HHV is 23.0 MJ/kg (5496 kcal/kg) and for olive core 18.7 to 22.1 MJ/kg [30, 44, 45]. Mean olive cake HHV is calculated at 4900 ± 430.9 kcal/kg (20.5 MJ/kg), and 4735.0 ± 21.7 kcal/kg (19.8 MJ/kg) for olive stone. In the olive residue samples, volatile content was about 90–95 % with a low ash content of about 5 %. However, these samples presented high levels of moisture which exceeded 50 %, ranging from 43–70 %. Suárez-García et al. have reported ash content of olive cake at about 10.9 % [30, 46] and 2.8 % [47] and that of volatile matter at 70.8 % [30, 46] and 62.1 % [47] slightly higher than the values measured in the collected samples.

Peach Residues

In peach core residues the mean HHV value was higher (4962 kcal/kg or 20.77 MJ/kg) than that of the other peach residues, i.e. peach pulp (4810 ± 500 kcal/kg) and peach peel (4551 ± 240 kcal/kg). Similar HHV values are reported by García et al. 19,590 ± 157 J/g, and in the Phyllis Database [30] (19.4–20.8 MJ/kg). Volatile content of peach core was estimated at about 95 % and low ash content under 1 %; however, peach pulp ash content exceeded 30 %. Nevertheless, these samples represent a good quality biomass source with medium moisture, and low Cl and S content.

Other Residues

Almond shell presented the lowest moisture content of 10 % with low ash, Cl and S content. In addition, high HHV were measured due to the low moisture content. García et al. [38] reported similar characteristics in almond shells, with a moisture content of 8.7 %, ash content of 2.2 % and HHV of

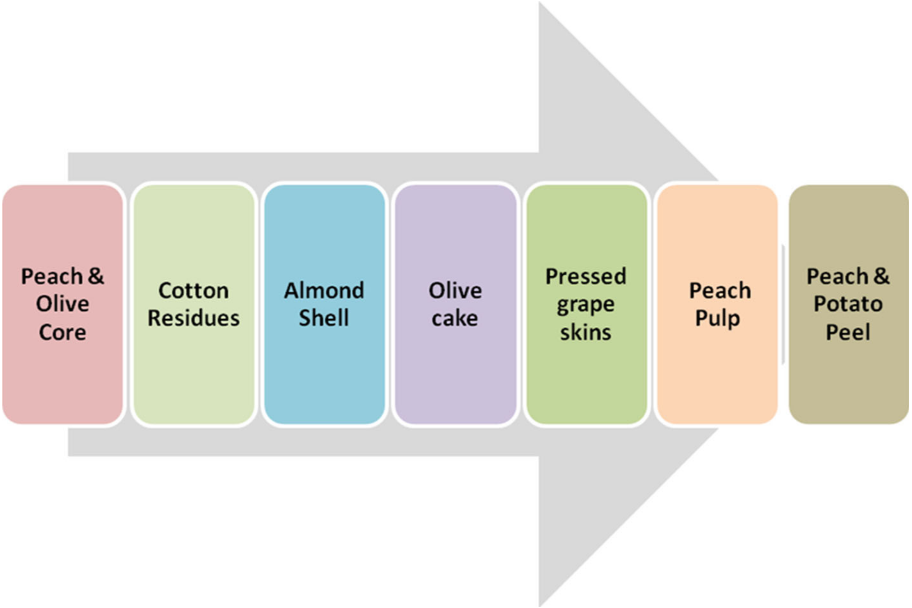

Fig. 5 Qualitative classification of the various biomass sources, in descending order

18.3 J/g. Potato peel samples presented very low HHV, 3969.6 ± 50.6 kcal/kg, due to high moisture content.

Based on the above quantitative and qualitative characteristics, these residues can be used for energy production or as pellets to produce electricity. Therefore the samples of peach and olive core and cotton residues represent the most promising biomass sources for energy utilization. These samples have high heating values and similar concentrations of volatiles. However, peach core has better characteristics than olive cake, with low moisture, ash, chlorine and sulfur content.

One of the main problems in the energy utilization of biomass by-products is the simultaneous production of large quantities of biomass residues in the same period (July–September). Consequently, oversized storage spaces in the processing units are required, further increasing the already high investment cost of the utilization facility; high infrastructure costs are associated with a high cost per tonne of output.

According to the survey, the residues from oil production are significant, including olive cake due to lack of local end users (olive cake factory), as are cotton mill residues. Another challenging biomass source represent the agricultural residues remaining in the farming area, such as olive and peach branches; these residues are usually disposed of by burning in the field, resulting in significant environmental impacts.

In conclusion, the qualitative classification in descending order of the examined types of biomass is shown in Fig. 5 according to their characteristic properties.

This classification may be used as a guide for the selection of the most appropriate fraction for energy utilization; however, two significant parameters have to be considered, i.e. the available quantity and the seasonal variation of biomass.

Conclusions

Knowledge of the energy properties of various biomass residues available in a particular area is a necessary tool for an efficient evaluation of their utilization potential. In addition to heating values, additional parameters have to be considered including moisture content, ash and volatiles, concentration of sulfur and chlorine, etc. According to the survey, a total of 1.33 million tonnes of fresh biomass residues are produced in the Central Macedonia Region of Greece. Biomass and particularly agricultural residues are produced in significant amounts, representing an important fraction of Central Macedonia Region's energy requirements; therefore, their energy utilization may contribute to the non- energy dependent development. The rational use and exploitation of biomass potential can lead to economically feasible solutions for regional agricultural industries. The qualitative classification in descending order of the examined types of biomass according to this survey is: core, cotton, shell, cake, grapes, pulp and peel. This prioritization is associated with the availability of materials (quantity) and their HHV values. Thus peach and olive core and cotton residues represent the most promising biomass sources for energy utilization. These materials have high heating values and similar concentrations of volatiles. However, peach core has better characteristics than olive cake, with low moisture, ash, chlorine and sulfur content. In conclusion, one of the main problems in the energy utilization of biomass by products is the simultaneous production of large quantities of biomass residues in the same period.

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