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Determination of calorific values of forest waste biomass by static bomb calorimetry

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Abstract

Calorific values of forest waste originating from forestry works such as woodland cleaning, reaforestation and, all other silviculture tasks, were measured by static bomb calorimetry. These waste materials, heretofore considered as useless refuse, are beginning to be used as alternative fuels in wide social sectors all over the world. Two of the main forest species, eucalyptus (*E. globulus* Labill) and pine (*P. pinaster* Aiton) existing in Galicia (NW Spain), are included in this study.

The experimental procedure was based on that proposed by Hubbard et al. [Experimental Thermochemistry, Interscience, New York, 1956, p. 5]. Simultaneously, some other parameters such as elementary chemical composition and heavy metal contents, moisture, density, and ash percentage after combustion in the bomb, were also determined. The experimental results, with calorific values exceeding 20 000 kJ kg^{-1}, make it advisable to use these materials as alternative fuels. The different parameters were measured using, as main equipment, a bomb calorimeter with an oxygen atmosphere, an elementary analysis equipment, and an atomic absorption spectrophotometer. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Calorific values; Forest waste; Alternative fuel; Energetic map; Xyloenergy

1. Introduction

In the last 50 years, continuous energy crisis around the world has slowed down the economic development of even rich industrialized countries. The excessive use of traditional fossil fuels is causing not only economic problems, but also ecological damages. At the same time, fossil fuel reserves are limited, thus making the search for alternative energy sources as a world wide top priority objective.

Within these alternative energy sources, the biomass, that is, the group of materials of biological origin capable of being used as xyloenergy sources is becoming an important one.

The present article is focused on the energetic evaluation of the forest biomass in Galicia (NW Spain) with the objective of its use as a rational and sustainable source. In our particular case, this objective is supported by the deep transformation of the forest environment in Galicia as a consequence of the introduction and exploitation of allochthonous forest species, such as *Eucalyptus globulus* Labill. This forest species is mainly used for the production of pulp.

This study is based on several physical, chemical, and biological parameters. Among these parameters, we shall emphasize the calorific value, that is, the

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amount of energy released by each unit of combustible mass. Two calorific values must be considered:

The higher heating value (HHV) is the amount of energy released by complete combustion of a mass unit of sample at constant volume in an oxygen atmosphere assuming that the final products of combustion consist of O_2, CO_2, SO_2, and N_2 in gas phase together with water that contained in the sample and that generated from the combined hydrogen in liquid form. This calorific value can be determined experimentally in the laboratory and that is one of the two main necessary parameters for calculation of risk indexes to be used for prevention of forest fires. For a given forest species, this value depends on the zone and season.

The lower heating value (LHV) can be calculated assuming that the water in the products remains in the form of vapor. The knowledge of LHV gives a realistic idea about the magnitude of a fire and becomes an index to quantify both the spread to neighboring surfaces and the virulence of forest fires. Also, the knowledge of LHV is very helpful to evaluate forest resources and to choose the best moment for their rational energetic exploitation.

Both calorific values are related through the equation

$$(\mathrm{LHV})_\mathrm{d} = (\mathrm{HHV})_\mathrm{d} - 24.42(9H_\mathrm{d}) \qquad (1)$$

where $(\mathrm{LHV})_\mathrm{d}$ corresponds to the lower calorific value of the dry sample $(\mathrm{HHV})_\mathrm{d}$ is the higher calorific value of the dry sample, and H_d the hydrogen percentage of the dry sample. The heat of vaporization of water is taken as 2441.8 $\mathrm{kJ\,kg^{-1}}$, and the water formed during combustion is nine times the hydrogen content.

Since a knowledge of chemical composition is necessary for calculation of calorific values, elementary chemical analysis (C, H, O, N, S, and Cl) and heavy metal composition (ppm) were also determined.

The exploitation of forest resources is done in the environment and not in the laboratory, for this reason, the climatic parameters (temperature, pluviosity, water availability, evapotranspiration, etc.) of the zone have a determinative influence on the start and spreading of fires. All these parameters can be represented together in the form of bioclimatic diagrams. These diagrams describe the area to be studied and have a direct influence on all the above-mentioned physico-chemical parameters. The use of these diagrams is very helpful for analysis of vegetative productivity periods and for comparison with calorific values, thus allowing the choice of the optimum period for energetic exploitation.

Combining LHV, physico-chemical, biological, and bioclimatic parameters allows the design of energetic maps.

All the studies were carried out in two different seasons (autumn and winter), in order to see how the changes in biological and bioclimatic characteristics influence the values obtained through the thermochemical parameters (LHV).

2. Experimental procedure

Previous to sampling, a forest zone was chosen and, on it, measurements of moisture, temperature, etc. were done. The zone was characterized according to type of soil, topography, orography, situation of the chosen forest species individual, other forest species existing in the zone, etc. All the observations were reflected in a form specially designed for this kind of study.

The first stage of experimental work begins with sampling. For this task, a homogeneous biomass zone in phase of exploitation was chosen. Within this zone, representative individuals of the forest species to be studied were elected. This election was made on the basis of the tree height that was measured by a hypsometer. The total volume of the tree was also measured.

Then, the tree was quartered and its residues were separated from timber-yielding wood. This usable wood part is generally used as raw material for pulp manufacturing. Forest residues were divided into three parts: leaves (aciculum, or needle in the case of pine trees), branches having a diameter less than 3 cm, and branches with a diameter in the range 3–6 cm.

The different samples were separately weighed, and then stored in labeled polypropylene bags to avoid loss of moisture during their transport to the laboratory. This transport should be done in a less than 8 h period.

Once in the laboratory, moisture contents of the raw samples were determined. Each sample was weighed to 0.1 or 1.0 g using a double-scaled Salter EP-22KA balance and then heated to constant weight in a Selecta 200210 natural desiccating stove. Humidity of the sample was determined as the weight loss of the sample after treatment in the stove. The dry sample was ground using two mills, a Retsch SM-1 and a Taunus MS-50, in order to homogenize the sample as much as possible before pressing the pellets to be used in the calorimetric experiments. Test samples were kept in a refrigerator in order to be used in reruns.

The final sample was divided into two fractions. Fraction A was used in the analyses to determine humidity, density and average composition. The samples were analyzed by a Perkin-Elmer atomic absorption spectrophotometer to determine their Cu, Cd, Zn, Pb and Mn contents and a Carlo Erba analysis equipment for determination of elementary composition C, H, O, N, S and Cl. The calorimetric experiments were performed using Fraction B. Sample pellets of about 1 g size [1] were placed in a stainless steel crucible introduced into a Parr-1108 sealed static bomb calorimeter made of Carpenter-20-Cb-3 special stainless steel. The experiments were performed at 25°C, following the method proposed by Hubbard et al. [2]. The bomb was filled with C-45 oxygen 99.99995% pure from Carburos Metálicos (Spain). The calorimeter was placed in an isothermal-jacket with an air-gap separation of 10 mm between all surfaces. Water was added to the calorimeter from a weighed glass vessel and for each experiment a correction to the energy equivalent was made for the deviation of the mass of water added from 4631 g weighed to 0.1 g. Temperature of this water was measured to 10^{-4} K at intervals of 15 s by a stable and sensitive platinum thermometer (ASL S 391/100) and recorded by a resistance bridge (ASL F-26) connected to a computer (Amstrad PC-2086/30). The water in the jacket was circulated by stirring and its temperature was maintained at 298.15 K by a Tronac PTC-41 temperature controller with a precision of 0.003°C over a week, and including a probe, a heater and cooling coil. The samples were ignited at (298.15 ± 0.01) K in oxygen at 3.04 MPa with 1 cm^3 of water added to the bomb. The electrical energy for ignition was determined from the change in potential across a 1256 or 2900 μF capacitor when discharged from about 40 V through a platinum wire. The pellet was connected to the ignition system by means of a cotton thread fuse, empirical formula $\mathrm{CH}_{1.686}\mathrm{O}_{0.843}$ with $-\Delta_c U_0 = 16250\,\mathrm{kJ\,kg}^{-1}$.

The samples, crucible, platinum wire, and cotton thread were weighed using a Sartorius R200D balance (sensitivity ± 0.01 mg). The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (BCS CRN-ISOP standard reference sample) from the Bureau of Analysed Samples Ltd., having a specific energy of combustion under standard bomb conditions of $26431.8 \pm 3.7\,\mathrm{J\,g}^{-1}$.The temperature rise measured in every experiment was corrected for stirring and exchange heating.

From five calibrations done with the bomb, the energy equivalent of the calorimeter was determined to be $E_0 = 22402.5 \pm 1.9\,\mathrm{J\,K}^{-1}$ (0.0085%), where the uncertainty quoted is the standard deviation of the mean.

3. Results and discussion

Main characteristics of the studied zone are given in Table 1. Climatic data shown in Table 1 are average values over the last 40 years [3] of those collected in the whole of the weather stations located in the area.

Table 1
Main characteristics of the studied zone in Galicia (NW Spain)[a]

Northern coast	
Altitude	0–100 m
Annual rainfall index	1012 mm
Summer rainfall index	140 mm
Mean annual temperature	13.9°C
Mean daily maximum temperature of the warmest month (July)	28°C
Hydric deficiency	171
Mediterraneanity index	2.11
Other species	*Quercus robur* L., *Castanea sativa* Miller and bush species

[a] Hydric deficiency is calculated from the difference between hydric availability and evapotranspiration in the dry period (summer). Mediterraneanity index is calculated from the ratio ETP/rainfall, in the same period, using appropriate tables.

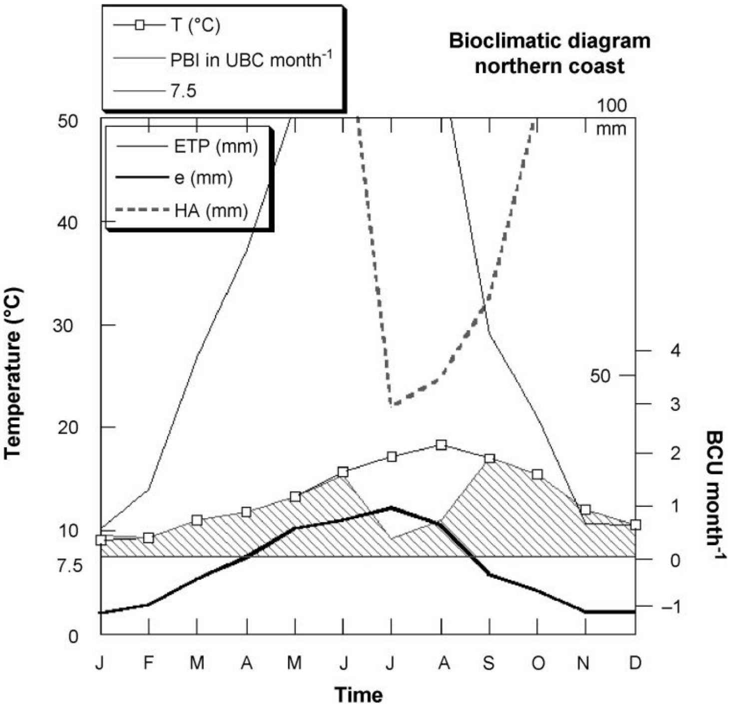

Fig. 1. Bioclimatic diagrams showing the main environmental characteristics of the northern coast zone of Galicia (NW Spain): *T* (temperature in °C), 7.5 (minimum temperature for vegetal activity), ETP (evapotranspiration in mm), *e* (residual evapotranspiration in mm), HA (hydric availability in mm), and PBI (potential bioclimatic intensity in BCU).

They are also represented on the bioclimatic diagram designed according to the method proposed by Montero and González [4] and shown in Fig. 1.

These characteristics were studied together with thermochemical parameters such as calorific values and values of density, moisture contents, bomb ashes after combustion, and chemical composition, to elaborate xyloenergy maps. The elaboration of this maps requires a complete knowledge of the study area as it depends not only on thermochemical parameters but also on physicochemical properties of the different species, biological characteristics, and parameters depending on physical environmental conditions.

Tables 2 and 3 show mean LHV and HHV corresponding to *E. globulus* Labill and *P. pinaster* Aiton, respectively. From these tables, it can be pointed out:

The ratio LHV/HHV decreases with moisture contents. This could be understood, according to Eq. (1), on the need of energy to evaporate water. Analysis of these tables shows that LHV/HHV ratio goes from 0.29 (63.4% of moisture) to 0.44 (45.3% of moisture). LHVs are also related to ash contents, the lower the ash contents the higher the LHV. However, these behavior could be overlapped by the stronger moisture effect. Finally, it can be also seen that HHV is bigger for leaves.

Tables 4 and 5 show the elementary chemical composition for the two species studied, some of these values could be necessary for calculation of calorific values.

As can be seen in Table 6, the mean LHV of the *E. globulus* Labill dead biomass sample, that is the forest residue usually abandoned ‘‘in situ’’ after forestry tasks, is higher than the mean LHV corresponding to raw residues (those produced immediately after cuts). This is a consequence of the loss of moisture experienced by the abandoned residues. However, HHV of raw residues are higher than those corresponding to dead biomass samples. This fact is easily

Table 2
Mean HHV, mean LHV, moisture, density, and ashes in bomb after combustion for *E. globulus* Labill corresponding to autumn and winter seasons, respectively

	Leaves	Branches ($\phi < 3\,\mathrm{cm}$)	Branches ($3\,\mathrm{cm} < \phi < 6\,\mathrm{cm}$)
Zone 1 — autumn			
LHV (kJ kg^{-1})	6151.90±65.98 (1.07%)	7657.38±66.82 (0.87%)	8068.44±155.27(1.92%)
HHV (kJ kg^{-1})	21165.08±169.18 (0.80%)	18391.47±131.29 (0.69%)	18352.92±283.87 (1.55%)
Density (kg m^{-3})	1070	990	1060
Moisture (%)	61.0	49.1	45.3
Bomb ashes (%)	1.67	0.32	0.46
Zone 2 — autumn			
LHV (kJ kg^{-1})	8239.09±56.20 (0.68%)	7519.37±94.56 (1.26%)	7352.64±34.90 (0.47%)
HHV (kJ kg^{-1})	21573.09±118.06 (0.55%)	18736.22±187.25 (1.00%)	19065.81±70.93 (0.37%)
Density (kg m^{-3})	1090	1000	1020
Moisture (%)	52.4	49.5	50.8
Bomb ashes (%)	0.74	0.43	0.23
Zone 1 — winter			
LHV (kJ kg^{-1})	7433.31±64.71 (0.87%)	7369.54±85.18 (1.16%)	7123.26±83.77 (1.18%)
HHV (kJ kg^{-1})	21572.98±146.73 (0.68%)	18818.44±170.35 (0.91%)	18187.02±165.88 (0.91%)
Density (kg m^{-3})	1050	990	930
Moisture (%)	55.9	50.0	49.5
Bomb ashes (%)	1.49	0.14	0.16
Zone 2 — winter			
LHV (kJ kg^{-1})	7820.98±20.61 (0.26%)	7615.98±116.57 (1.53%)	7601.19±91.35 (1.20%)
HHV (kJ kg^{-1})	21583.23±44.61 (0.21%)	18449.32±222.45 (1.21%)	18344.35±175.67 (0.96%)
Density (kg m^{-3})	960	910	1020
Moisture (%)	53.8	47.6	48.0
Bomb ashes (%)	1.88	0.41	0.55

Table 3
Mean HHV, mean LHV, moisture, density, and ashes in bomb after combustion for *P. pinaster* Aiton corresponding to autumn and winter seasons, respectively, for live matter

	Needles	Branches ($\phi < 3\,\mathrm{cm}$)	Branches ($3\,\mathrm{cm} < \phi < 6\,\mathrm{cm}$)
Zone 1 — autumn			
LHV (kJ kg^{-1})	6655.32±92.29 (1.39%)	10320.17±193.27 (1.87%)	4779.86±98.22 (2.05%)
HHV (kJ kg^{-1})	21685.78±231.30 (1.07%)	20532.30±324.83 (1.58%)	19638.17±284.69 (1.45%)
Density (kg m^{-3})	935	797	784
Moisture (%)	60.1	40.5	65.5
Bomb ashes (%)	0.34	0.07	0.09
Zone 2 — winter			
LHV (kJ kg^{-1})	5780.43±50.70 (0.88%)	8433.23±105.40 (1.25%)	7127.52±38.95 (0.55%)
HHV (kJ kg^{-1})	21144.85±134.85 (0.64%)	20545.74±206.27 (1.00%)	19534.07±82.87 (0.42%)
Density (kg m^{-3})	1087	947	878
Moisture (%)	63.4	48.9	53.0
Bomb ashes (%)	0.69	0.24	0.15

Table 4
Chemical analysis for live matter of *E. globulus* Labill

	Leaves	Branches ($\phi < 3\,\mathrm{cm}$)	Branches ($3\,\mathrm{cm} < \phi < 6\,\mathrm{cm}$)
Zone 1 — autumn			
C (%)	57.66	52.75	52.63
H (%)	7.15	6.97	7.19
O (%)	34.17	40.01	39.58
N (%)	0.69	0.18	0.17
S (%)	0.33	0.09	0.43
Zone 2 — autumn			
C (%)	58.92	55.21	53.37
H (%)	7.17	6.61	7.28
O (%)	33.07	37.84	38.86
N (%)	0.70	0.20	0.24
S (%)	0.14	0.14	0.25
Zone 1 — winter			
C (%)	57.85	53.04	52.19
H (%)	7.38	7.45	7.68
O (%)	32.89	39.24	39.82
N (%)	1.57	0.14	0.15
S (%)	0.31	0.13	0.16
Zone 2 — winter			
C (%)	54.65	51.57	51.88
H (%)	8.24	7.72	6.70
O (%)	35.88	40.35	41.09
N (%)	0.92	0.19	0.17
S (%)	0.31	0.17	0.16

understandable as a consequence of the high content of resins, essential oils, and other volatile compounds, with calorific values higher than 40000 kJ kg^{-1} [5], that are lost for abandonment of dead matter due to the action of environmental and climatic agents.

Table 7 gives mean LHV corresponding to pine trees. Owing to the lack of data for dead matter of *P. pinaster* Aiton, data corresponding to the different conifers existing in the zone, that show a similar behavior, were used.

Table 5
Chemical analysis for live matter of *P. pinaster* Aiton

	Needles	Branches ($\phi < 3\,\mathrm{cm}$)	Branches ($3\,\mathrm{cm} < \phi < 6\,\mathrm{cm}$)
Zone 1 — autumn			
C (%)	55.23	55.42	54.92
H (%)	6.04	6.94	5.22
O (%)	36.01	37.19	39.48
N (%)	2.06	0.23	0.16
S (%)	0.66	0.22	0.22
Zone 2 — winter			
C (%)	55.12	55.29	54.67
H (%)	7.82	7.76	7.35
O (%)	35.32	36.38	37.68
N (%)	1.59	0.52	0.22
S (%)	0.15	0.05	0.08

Table 6
Mean LHV and HHV of *E. globulus* Labill

E. globulus Labill	LHV ($kJ\ kg^{-1}$)	HHV ($kJ\ kg^{-1}$)	Moisture (%)
Live matter	7476.44	20139.89	47.2–54.7
Dead matter	9104.51	19821.48	28.6–40.0

Table 7
Mean LHV and HHV of *P. pinaster* Aiton and other conifers

	LHV ($kJ\ kg^{-1}$)	HHV ($kJ\ kg^{-1}$)	Moisture (%)
P. pinaster Aiton			
Live matter	7568.01	20588.66	40.5–60.5
Other conifers			
Live matter	8557.46	21079.09	50.8
Dead matter	9124.57	20756.05	41.5

Table 8 shows exploitation criteria [6] used for calculation of available electric energy from forest residues originating from forestry tasks. By accepting these criteria, and assuming a yield of 25% for this type of energy transformation plants, a yearly generation of 5×10^9 kW h was calculated. This amount constitutes about 3% of the total electric energy generated in Spain in a year. Considering a price of 0.04 Euros/kW h, a total amount of 210×10^6 Euros per year can be obtained, which is about the investment in Spain to prevent and extinguish forest fires.

The energetic maps shown in Fig. 2 were elaborated using LHVs listed in Tables 2 and 3. Zones with no forestry, or occupied by other species, are also shown. Analysis of the mentioned tables shows that *E. globulus* Labill present higher exploitation values in winter ($7646.5\ kJ\ kg^{-1}$, class 4) than in autumn ($7337.3\ kJ\ kg^{-1}$, class 3). On the other hand, *P. pinaster* Aiton shows class 4 values ($8059.8\ kJ\ kg^{-1}$) in autumn, and class 3 ($7076.2\ kJ\ kg^{-1}$) in winter. Class energetic values were assigned after analysis of the different forest species existing in Galicia [7–14]. These values do not agree with previous classifications [5] corresponding to different zones. Because of that it was decided to elaborate a new classification for forest species in Galicia. Energetic maps may become very helpful to design sustainable exploitation campaigns of the energetic resources existing in forest biomass.

4. Conclusions

From the previously shown data, it can be concluded that an energetic exploitation of forest residues is viable owing to:

- The continuous and regular availability of enough combustible materials.
- The existence of available technology of frequent use in industry to transform calorific energy into electric energy.
- The electric energy obtained from xyloenergy is considered as a clean and high-quality energy.
- From the economic point of view these kind of enterprises are well considered owing to the great demand for energetic sources.

At the same time, the use of these residual resources yields a twofold benefit. On the one hand, the above-mentioned economic benefit, on the other hand, an ecological benefit because the removal of forest residues diminishes the risk of initiation and spreading of forest fires. In Galicia, accumulation of forest residues is the main cause of all kind of forest fires. It must be

Table 8
Exploitation criteria [14] and theoretical values of electricity production

Occupied surface (ha)	Trees ha^{-1}	Forest residues (kg per tree)	Cutting periods (year)	kW h	Euros
P. pinaster Aiton					
550 000	2000	99.8	20	2.87×10^9	121.8×10^6
E. globulus Labill					
250 000	2500	98.4	15	2.1×10^9	89.6×10^6

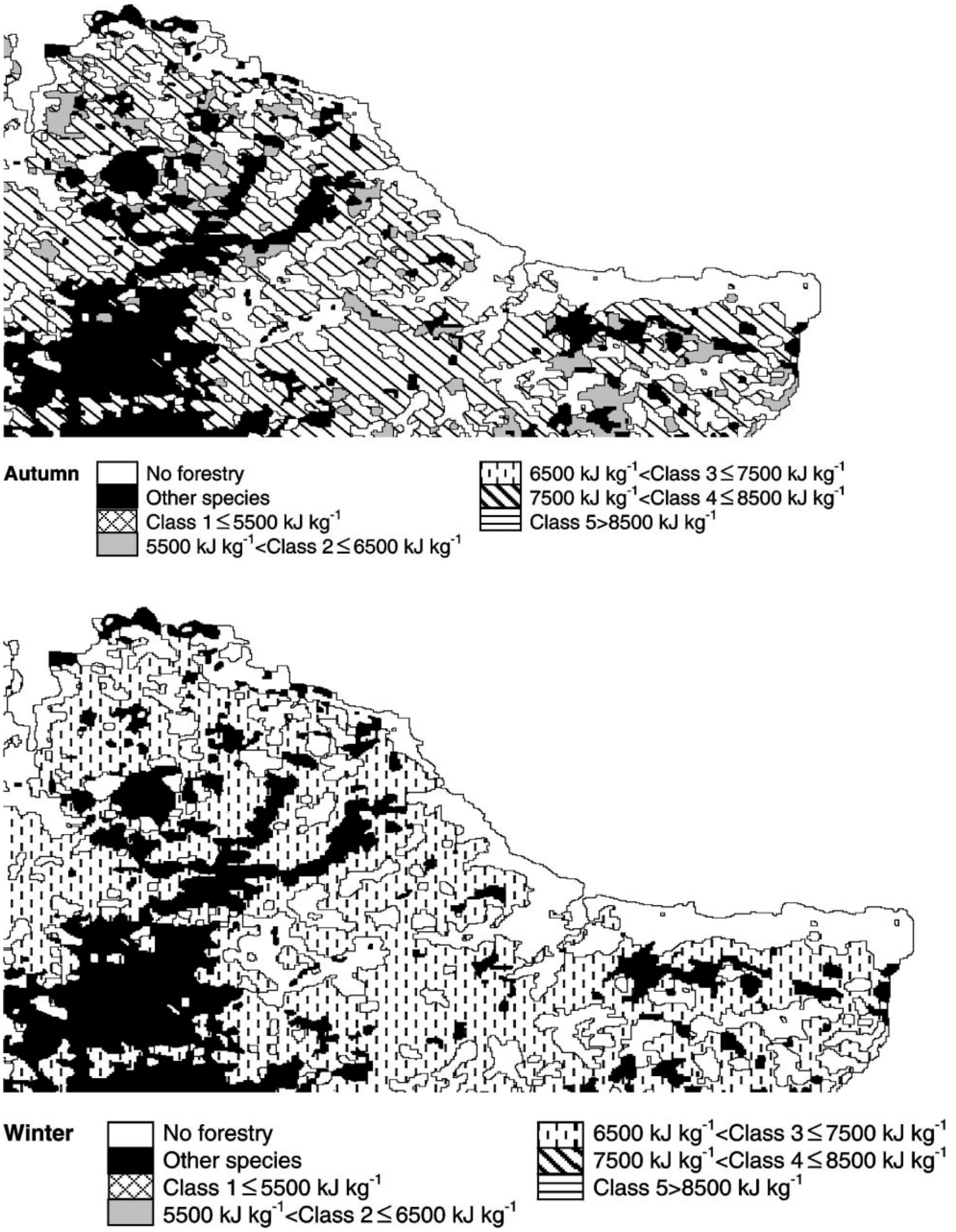

Fig. 2. Energetic map of the northern coast zone of Galicia corresponding to autumn and winter season, respectively.

said that residues removal should be done in a rational way to avoid defertilizing phenomena that could be originated by an excessive cleaning campaign.

Finally, we considered that elaboration of energetic maps is a basic tool to design forest resources exploitation sustainable campaigns.

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