

ENERGETIC EVALUATION OF BIOMASS ORIGINATING FROM FOREST WASTE BY BOMB CALORIMETRY

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Abstract

Calorific values and flammability changes during a year for forest waste originating from silviculture task in Galicia (NW Spain) are reported. These waste materials are becoming to be used as alternative fuels.

The present study was made on several hardwood forest species. These forest species occupy nowadays approximately 30% of the total forest surface of Galicia.

Calorific values were measured by static bomb calorimeter in an oxygen atmosphere. Flammability was determined using a standard epiradiator. Simultaneously, some other parameters such as elementary chemical composition, heavy metal contents, moisture, density, ash percentage after combustion in the bomb, and main bioclimatic characteristics, were also determined.

Keywords: alternative fuel, calorific value, flammability, forest waste, xyloenergy

Introduction

In the last 25 years the forest sector in Galicia (NW Spain) suffered a deep transformation. Due to abandonment, the land traditionally devoted to forest cultivate was taken by bush, nowadays, cover more than 1 200 000 ha [1]. The abandonment of forest land originated from different sources. Among these:

1. A large increase in forest wildfires that devastated more than 1 000 000 ha.
2. The introduction of new allochthonous species mainly eucaliptus (*E. globulus Labill*).
3. Abandonment of agriculture task, thus breaking the traditional agriculture-cattle equilibrium.

As a result of the interaction among these 3 factors, the surface of productive soil has decreased and, at the same time, the generation of forest residues increased.

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These forest wastes, nowadays abandoned in situ as useless refuse, are mainly responsible for forest fires. However, they can be used as alternative energy sources.

In the present study, we focussed on a twofold objective. On the one hand an economical one, as this residual biomass can be transformed into a fuel useful as an alternative energy source. On the other hand, from the ecological point of view, a rational and sustainable exploitation of these energetic resources can help to prevent and/or minimize forest fires.

The thermochemical study of different species is based on the calculation of their calorific values through experiments carried out in a static bomb calorimeter following the procedure proposed by Hubbard *et al.* [2], and of flammability using the procedure and tables set up by Valette [3].

Calorific value can be defined as the amount of energy released by a mass 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 O₂, CO₂, SO₂, and N₂ in gas phase together with water, that the sample contains and that generated from the combined hydrogen, in a liquid form. This calorific value can be determined experimentally in the laboratory and because of this, it is one of the two main parameters used for calculation of risk indexes, which are very useful for fire prevention.

The lower heating value (*LHV*) can be calculated from *HHV* assuming that water in the products remains in the form of vapor. Knowing *LHV* is very helpful to evaluate forest resources from the energetic point of view.

Both calorific values are related through the equation:

$$(LHV)_d = (HHV)_d - 24.42(9H_d) \quad (1)$$

where $(LHV)_d$ corresponds to the lower calorific value of the dry sample, $(HHV)_d$ is the higher calorific value of the dry sample, and H_d is the hydrogen percentage of the dry sample. The heat of vaporization of water is taken as 2441.8 kJ kg⁻¹, and the water formed during combustion is 9 times higher than the hydrogen content (%).

The flammability can be defined as the easiness of a material to catch fire both spontaneously or through exposition to certain ambiances.

The rest of the parameters studied were: the elementary chemical composition (C, H, O, N and S), as well as Cl, and heavy metals (Cu, Cd, Mn, Pb and Zn), moisture content, density of the different forest species and ash percentage after combustion in the bomb.

All these thermochemical parameters undergo the influence of the climatic conditions of the area. For this reason, the bioclimatic diagram [4–5] of the zone where the sample was collected must be taken into account. This bioclimatic diagram includes a lot of climatic features of the area (temperature, pluviosity, vegetative productivity, different bioclimatic indices, potential evapotranspiration, etc.), having a decisive influence on all the above parameters and is a key to an accurate interpretation of the results.

All the studies were carried out during one year.

Method

Prior to sampling, a forest zone was chosen and measurements of moisture, temperature, etc. were made. 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 recorded in a form specially designed in our group for this kind of study.

The samples were collected from a previously chosen 1 ha of forest. The plots were divided into 1 m² size sites, five of which were randomly chosen. From every site, bulk samples consisting of bark, branches having a diameter not greater than 8 cm, from pruning of trees, fruits, leaves and, in general, all of the living parts of trees were collected. This bulk sample was reduced by a coning and quartering procedure to a representative sample of about 1 kg.

One part of this sample was used in the flammability experiments which were performed, following the standard UNE-23-721, using a standard epiradiator of 500 W constant nominal power. Flammability values were obtained according to the tables proposed by Valette [3].

The remaining sample was weighed to 0.1 or 1.0 g using a double scaled Salter EP-22KA balance and then left for 12 h in a Selecta 200210 natural desiccating stove. Humidity of the sample was determined as the mass loss of the sample after treatment in the stove.

Once the humidity was determined, the sample was ground using two mills of different power, a Retsch SM-1 blade mill and a Taunus MS-50 grinder, in order to homogenize the sample as much as possible, thus making easier the preparation of the sample pellets to be used in the calorimetric experiments.

A part of this ground sample, labelled as fraction A, was used to measure density and average chemical composition of each of the species being studied. The samples were analyzed using a Carlo Erba analysis equipment for determination of elementary composition (C, H, N, O and S) and a Perkin Elmer atomic absorption spectrophotometer to determine heavy metal contents (Cu, Cd, Zn, Pb, Mn and Cl). A second fraction named B was used to determine calorific values and ash percentage after combustion of the different species. All the combustion experiments were made in a static bomb calorimeter, a sealed Parr-1108, following the procedure described by Hubbard *et al.* [2]. Sample pellets of about 1 g size [6] were put in a stainless steel crucible and then inside the bomb. A cotton thread fuse of empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$ was attached to the platinum ignition wire and placed in contact with the pellet. In all the experiments the bomb was filled with C-45 oxygen 99.99995% pure from Carbueros Metálicos (Spain) at 3.04 MPa. Ignition was at 298.15 K with 1.0 cm³ of water added to the bomb. The calorimeter was placed in an isothermal jacket with an air-gap separation of 10 mm between all surfaces. 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 bomb calorimeter was submerged in a calorimeter can filled with 4631 g of distilled water weighed by a Mettler P-11 balance (sensitivity ± 0.1 g). A correction to

the energy equivalent was made for the deviation of the mass of water to 4631 g. The calorimeter jacket was maintained at constant temperature by circulating water kept at 25°C by a Tronac PTC-41 temperature controller, with a precision of 0.003°C per week, including a probe, a heater and cooling coil. The water temperature was kept homogeneous in the whole calorimeter by means of two motors which continuously stirred both the calorimetric tank and the calorimeter. Temperature changes taking place in the calorimeter can during the experiments were followed by an Isotech 935-14-13 platinum resistance thermometer connected to an ASL F-26 resistance bridge. Temperature data were taken every 15 s and recorded by a 2086 Amstrad computer. The ignition of the sample was achieved on step 80, through the discharge of the capacitor. This ignition started the main period of the calorimetric run. The experiment ended at step 240. The bomb calorimeter was removed from the can and after being carefully open, ash and water resulting from the combustion were evaluated following routine procedures. The corrected temperature rise was obtained using a computer program and the measured data. Knowledge of this temperature rise allows the calculation of calorific values.

The equivalent energy of the calorimeter was determined using the combustion of benzoic acid, BCS CRN-ISOP standard reference sample from Bureau of Analysed Samples Ltd, having an energy of combustion under standard bomb conditions of $26431.8 \pm 3.7 \text{ kJ kg}^{-1}$. From five calibration experiments $E(\text{calor}) = 22402.5 \pm 1.9 \text{ J K}^{-1}$ (0.0085%), where the uncertainty quoted is the standard deviation of the mean.

The temperature rise was corrected for stirring and exchange heating.

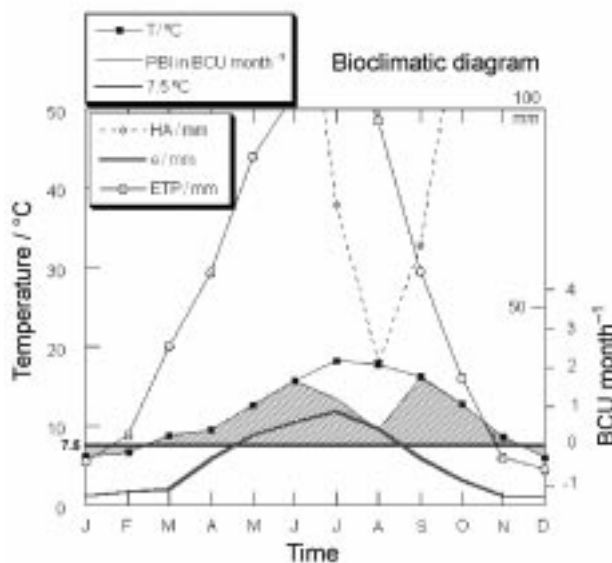


Fig. 1 Bioclimatic diagrams showing the main environmental characteristics of the zone studied: T (temperature in °C), 7.5 (minimum temperature for vegetal activity), ETP (evapotranspiration in mm), e (residual evapotranspiration in mm), HA (hydric availability in mm) and PBI (potential bioclimatic intensity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

Results and discussion

The results reported in different tables and figures correspond to the seasonal evolution of physicochemical parameters during the year as a function of climatic and biological parameters and the state of the different species.

The main characteristics of the zone studied, which is representative of 70% of Galicia (NW Spain) landscape, are shown in Table 1 [5]. Climatic data listed in this table are average values over the last 40 years [3] of those collected in the whole of the weather stations located in the area. These data together with some other biological parameters available from literature were used to construct the bioclimatic diagram shown in Fig. 1.

Table 1 Main bioclimatic and biological parameters [5]

Altitude: 100–550 m.
Annual rainfall index: 1090 mm.
Summer rainfall index: 122 mm.
Mean annual temperatura: 11.6°C.
Mean daily maximum temperature of the warmest month (July): 35.07°C.
Hydric deficiency: 178.
Mediterraneanity index: 2.23
Representative species [1] of the zone:
Hardwoods: <i>Acer pseudoplatanus</i> L., <i>Alnus glutinosa</i> (L.) Gaertner, <i>Betula pendula</i> Roth., <i>Quercus pyrenaica</i> Willd., <i>Quercus robur</i> L. and <i>Salix atrocinera</i> L.

Table 2 shows mean seasonal HHV , LHV , moisture content ($M\%$), density (D), and ash percentage after combustion in the bomb (BA) of the different species existing in the zone [7–12]. Analysis of data shows that the ratio LHV/HHV decreases with the moisture content. This could be understood, according to Eq. (1), on the need of energy to evaporate water. Values of LHV/HHV go from 0.19 (70.66% of moisture) to 0.58 (33%). $LHVs$ are also related to both ash and hydrogen contents. However, this behaviour could be overlapped by the stronger moisture effect.

Elementary composition (%) for seven species studied are shown in Table 3 [7–12]. Some of these values (C, H, S) could be used to estimate calorific values using stoichiometric relationships and energetic data available from literature. As it was pointed out in a previous article [13], trees are very important models of forest pollution. For this reason, the detection of all heavy metals constitutes a basic reference. Table 3 shows also heavy metal contents that can give an idea of pollution behaviour in case of wildfires. Contents of Mn are very high compared to the other elements studied. This fact can be explained on the need for this element in the transfer from water, electron donor, to the photosystem II (for the formation of one oxygen molecule, four electrons must be separated from two water molecules). This process needs the presence of Mn^{2+} and chloride ions [14].

Table 2 Mean high heating values (*HHV*) and mean low heating values (*LHV*), moisture (*M*), density (*D*), and ash percentage after combustion in the bomb (*BA*), of the different species along the seasons of the year in the zone [7–12]

	<i>HHV</i> /kJ kg ⁻¹	<i>LHV</i> /kJ kg ⁻¹	<i>M</i> /%	<i>D</i> /kg m ⁻³	<i>BA</i> /%
<i>Acer pseudoplatanus</i> L.					
Spring	17795±71 (0.40%)	6363±36 (0.57%)	49.31	890	4.62
Summer	17848±74 (0.42%)	5052±29 (0.58%)	60.50	820	2.67
Autumn	18436±27 (0.15%)	5498±11 (0.22%)	56.25	810	2.13
Winter	17834±12 (0.07%)	8747±7 (0.08%)	41.00	820	1.15
<i>Alnus glutinosa</i> (L.) Gaertner					
Spring	21090±121 (0.58%)	6051±46 (0.77%)	61.54	790	0.48
Summer	21073±90 (0.43%)	4020±26 (0.66%)	70.66	840	1.44
Autumn	20628±90 (0.44%)	5014±31 (0.63%)	65.44	800	0.24
Winter	19861±74 (0.38%)	6703±32 (0.49%)	56.32	800	0.24
<i>Betula pendula</i> Roth.					
Spring	20755±131 (0.63%)	6863±56 (0.82%)	57.14	770	0.46
Summer	21086±24 (0.12%)	6534±10 (0.15%)	59.30	850	0.86
Autumn	20522±64 (0.31%)	8668±32 (0.38%)	48.51	840	0.37
Winter	19837±147 (0.74%)	7696±71 (0.93%)	51.62	780	0.18
<i>Castanea sativa</i> Miller					
Spring	17460±58 (0.34%)	5363±24 (0.46%)	58.08	610	1.58
Summer	17436±86 (0.50%)	5458±36 (0.67%)	57.49	590	2.18
Autumn	17130±85 (0.50%)	8515±51 (0.60%)	40.00	590	1.71
Winter	18667±50 (0.27%)	7334±25 (0.35%)	50.00	600	0.30
<i>Quercus pyrenaica</i> Willd.					
Spring	19166±35 (0.19%)	8248±18 (0.23%)	47.64	1020	1.14
Summer	19394±80 (0.41%)	10574±51 (0.48%)	36.36	930	1.20
Autumn	19254±59 (0.31%)	11195±39 (0.35%)	33.33	800	1.70
Winter	18893±33 (0.18%)	9981±20 (0.21%)	38.05	900	1.52
<i>Quercus robur</i> L.					
Spring	17627±45 (0.26%)	4297±17 (0.41%)	61.36	640	0.66
Summer	18541±78 (0.42%)	7794±41 (0.53%)	47.80	620	2.28
Autumn	17468±10 (0.06%)	6654±5 (0.08%)	51.00	630	1.42
Winter	18112±54 (0.30%)	5451±22 (0.42%)	58.16	640	2.53
<i>Salix atrocinera</i> L.					
Spring	20185±113 (0.56%)	7012±50 (0.72%)	55.46	810	1.18
Summer	21341±142 (0.67%)	7001±60 (0.86%)	57.64	800	0.75
Autumn	19670±106 (0.54%)	6952±48 (0.69%)	54.62	790	0.47
Winter	19030±115 (0.61%)	6694±52 (0.78%)	54.81	720	0.22

Table 3 Results of chemical analysis and volatile metals for dry sample [7–12]

	Chemical analysis/% of total composition						Volatile metals/ppm				
	N	C	H	O	S	Cl	Cu	Cd	Zn	Pb	Mn
<i>A. pseudoplatanus</i> L.											
Spring	2.66	45.45	13.04	38.70	0.15	–	13.12	1.13	28.15	1.01	891.32
Summer	1.77	45.00	5.99	46.93	0.23	0.08	18.13	1.65	39.00	1.65	2044.50
Autumn	1.95	47.92	12.42	37.61	0.10	–	17.12	1.10	41.80	4.10	160.30
Winter	2.01	46.96	5.97	44.88	0.18	–	7.82	1.06	24.37	7.20	90.00
<i>A. glutinosa</i> (L.) Gaertner											
Spring	2.07	51.65	6.59	39.62	<0.01	0.06	15.75	1.97	111.24	29.53	63.98
Summer	3.10	50.98	6.77	39.09	<0.01	0.06	17.90	0.99	84.55	6.96	13.93
Autumn	1.22	50.92	6.80	41.00	<0.01	0.05	9.77	<0.01	45.92	8.79	6.84
Winter	1.48	50.25	6.22	41.99	<0.01	0.05	14.19	2.03	95.39	19.26	49.67
<i>B. pendula</i> Roth.											
Spring	1.21	56.64	6.77	35.33	<0.01	0.05	14.11	2.02	109.86	21.17	36.28
Summer	1.99	51.54	6.71	39.71	<0.01	0.04	11.50	2.87	158.18	1.92	103.53
Autumn	0.81	47.59	6.31	45.25	0.01	0.03	9.36	<0.01	37.46	10.41	4.16
Winter	0.68	46.92	6.02	46.32	<0.01	0.04	39.12	1.86	149.95	18.63	37.25
<i>C. sativa</i> Miller											
Spring	0.86	45.60	5.84	47.49	0.16	0.05	8.03	3.20	35.33	2.10	63.70
Summer	1.98	45.71	5.89	45.97	0.26	0.19	160.72	1.96	25.50	3.92	4704.00
Autumn	2.53	47.16	5.96	44.24	0.11	–	9.31	1.35	30.21	3.21	1931.10
Winter	2.26	48.28	7.08	42.29	0.10	–	4.70	–	18.32	1.40	2212.31

Table 3 Continued

	Chemical analysis/% of total composition						Volatile metals/ppm				
	N	C	H	O	S	Cl	Cu	Cd	Zn	Pb	Mn
<i>Q. pyrenaica</i> Willd.											
Spring	1.83	45.43	5.42	47.20	0.12	>0.01	43.00	<1.00	133.00	25.00	114.00
Summer	1.55	46.86	6.29	45.16	0.14	>0.01	18.00	<1.00	93.00	4.00	311.00
Autumn	0.76	47.14	5.65	46.33	0.08	0.04	31.00	<1.00	66.00	18.00	75.00
Winter	1.42	47.73	5.83	44.86	0.06	0.10	16.00	<1.00	36.00	4.00	89.00
<i>Q. robur</i> L.											
Spring	3.05	44.70	11.96	40.14	0.15	8.71	6.50	1.85	18.51	0.60	293.50
Summer	1.82	45.88	6.25	45.66	0.25	0.14	75.05	3.26	21.30	1.63	3100.00
Autumn	1.97	45.87	6.12	45.96	–	0.08	6.30	1.00	18.31	0.40	295.80
Winter	1.16	46.87	7.69	44.10	0.15	0.03	8.42	3.37	16.84	0.80	397.40
<i>S. atrocinera</i> L.											
Spring	1.79	50.13	6.37	41.62	<0.01	0.07	17.18	2.02	119.27	40.43	44.47
Summer	1.89	52.00	6.79	39.25	<0.01	0.07	12.76	2.95	95.25	<1.00	62.85
Autumn	1.25	49.89	6.42	42.37	0.01	0.07	27.00	1.93	165.89	7.72	59.78
Winter	0.82	48.42	5.71	44.97	0.01	0.07	20.30	2.53	125.64	31.73	71.07

Flammability [3] and *LHV* [11] values, and their evolution during the seasons of the year, corresponding to the species studied are shown in Table 4. As it can be seen, flammability values are higher in summer as a consequence of climatic conditions (high temperature and low moisture content). However, *LHV* increases in autumn and winter. This can be understood based on the fact that most of these species show their blooming periods in spring or summer.

Table 4 Flammability values according to the model proposed by Valette [3], and *LHV* class [11]

Flammability class	Spring	Summer	Autumn	Winter
<i>A. pseudoplatanus</i> L.	3	5	4	3
<i>A. glutinosa</i> (L.) Gaertner	1	2	1	1
<i>B. pendula</i> Roth.	1	2	2	1
<i>C. sativa</i> Miller	4	5	5	4
<i>Q. pyrenaica</i> Willd.	1	5	4	2
<i>Q. robur</i> L.	5	5	4	4
<i>S. atrocinera</i> L.	1	2	2	1

Flammability class: class 0: very low flammability, class 1: low flammable, class 2: flammable, class 3: moderately flammable, class 4: very flammable, and class 5: extremely flammable

<i>LHV</i> class	Spring	Summer	Autumn	Winter
<i>A. pseudoplatanus</i> L.	3	2	2	5
<i>A. glutinosa</i> (L.) Gaertner	3	1	2	4
<i>B. pendula</i> Roth.	4	4	5	5
<i>C. sativa</i> Miller	2	2	5	4
<i>Q. pyrenaica</i> Willd.	5	5	5	5
<i>Q. robur</i> L.	1	5	4	2
<i>S. atrocinera</i> L.	4	4	4	4

LHV classes: class 1: $LHV < 4500 \text{ kJ kg}^{-1}$; class 2: $LHV \geq 4500 \text{ kJ kg}^{-1}$ and $< 5500 \text{ kJ kg}^{-1}$, class 3: $LHV \geq 5500 \text{ kJ kg}^{-1}$ and $< 6500 \text{ kJ kg}^{-1}$; class 4: $LHV \geq 6500 \text{ kJ kg}^{-1}$ and $< 7500 \text{ kJ kg}^{-1}$, class 5: $LHV \geq 7500 \text{ kJ kg}^{-1}$

Different criteria used for economical and energetic evaluation are reported in Table 5.

From data recorded in different tables and those available from the 2nd Spanish Forest Inventory edited by the Spanish Agriculture Department, energetic maps, such as those shown in Fig. 2, can be designed.

Conclusions

A fuel is considered self-sufficient, that does not need auxiliary fuels, when its calorific value is $> 4200 \text{ kJ kg}^{-1}$. Because of this, forest residues originated from the forest species studied, with mean *LHV*s higher than 7000 kJ kg^{-1} can be considered as a

Table 5 Exploitation criteria and theoretical values of electricity production

Hardwood species	Ha	Forest waste/ kg year ⁻¹	Mean <i>LHV</i> / kJ kg ⁻¹	Kcal/ kWh	Efficiency	Euros
<i>A. pseudoplatanus</i> L.			6415.45			
<i>A. glutinosa</i> (L.) Gaertner			5447.62			
<i>B. pendula</i> Roth.	94000		7440.55			
<i>C. sativa</i> Miller		2.5	6667.83	1.163·10 ⁻³	25%	0.04 E kWh ⁻¹
<i>S. atrocinera</i> L.			6914.99			
<i>Q. pyrenaica</i> Willd.	101000		10000.07			
<i>Q. robur</i> L.	208000		6049.37			
Total	403000	1.6·10 ⁹	7169.02			3.3·10 ⁷

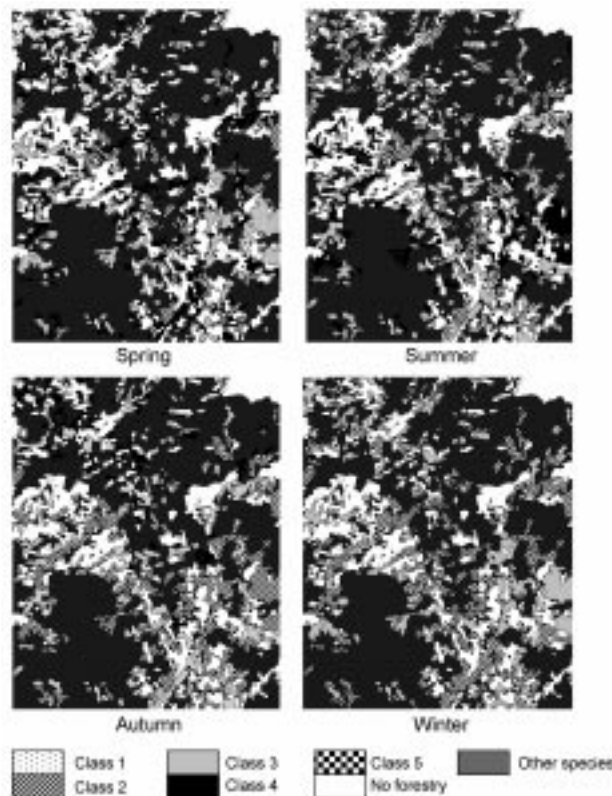


Fig. 2 Seasonal evolution of energetic values of forest residues corresponding to different species studied

valuable source of alternative energy. At the same time, the regular generation of these materials make them a sustainable source. Analysis of different data shows that autumn must be considered as the optimum exploitation period because in this season the materials are abundant, moisture contents decrease thus increasing *LHV*s, flammability values are high, the vegetal activity slows down, and also because the withdrawal of these residues will prevent the risk of wildfires in spring and summer.

From the economical point of view, retrieval of forest residues could originate a benefit of $3.3 \cdot 10^7$ euros per year. This result was worked out on the following basis:

1. Hardwood species occupy 403 000 ha, with a population of 1600 trees per ha, and a generation of 5 kg per tree, only 2.5 kg of which are collected in order to avoid soil defertilization.
2. Mean *LHV* is about 7200 kJ per kg.
3. An efficiency of 25% for the energetic transformation is assumed.
4. For calculation, a price of 7 pesetas (0.04 euros) per kWh is assumed.

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References

- 1 Tercer Inventario Forestal Nacional 1997–2006. Ed. Ministerio de Medio Ambiente, Madrid 1993.
- 2 W. Hubbard, D. Scott and G. Waddington, *Experimental Thermochemistry*. Ed. F. D. Rossini Interscience Publishers Inc., New York 1956, p. 5.
- 3 J. Ch. Valette, *Documantos del seminario sobre métodos y equipos para la prevención de incendios forestales*. ICONA, Madrid 1988.
- 4 J. L. Montero de Burgos and J. L. González Rebollar, *Diagramas Bioclimáticos*, ICONA, Madrid 1983.
- 5 *Resumo de Datos Climatolóxicos de rede das Estacións do Centro de Investigacións Forestais de Lourizán 1955–1994*, Ed. Xunta de Galicia, Consellería de agricultura, Gandería e Montes, Santiago de Compostela 1995.
- 6 D. Wagman, W. Evans, V. Parker, R. Schumm, L. Halow, S. Bailey, K. Churney and R. J. Nuttall, *Phys. Chem. Ref. Data*, (1982) 11.
- 7 L. Núñez-Regueira, J. Proupín Castiñeiras and J. A. Rodríguez-Añón, *Bioresource Technol.*, 57 (1996) 283.
- 8 L. Núñez-Regueira, J. Rodríguez-Añón and J. Proupín-Castiñeiras, *Bioresource Technol.*, 61 (1997) 111.
- 9 L. Núñez-Regueira, J. Rodríguez-Añón and J. Proupín-Castiñeiras, *Bioresource Technol.*, 69 (1999) 23.
- 10 L. Núñez-Regueira J. Rodríguez-Añón, J. Proupín-Castiñeiras and B. Mouriño, *Thermochim. Acta*, 328 (1999) 111.
- 11 L. Núñez-Regueira, J. Rodríguez-Añón and J. Proupín-Castiñeiras, *Bioresource Technol.*, 71 (2000) 51.
- 12 L. Núñez-Regueira, J. Rodríguez-Añón and J. Proupín-Castiñeiras, *Thermochim. Acta*, 349 (2000) 103.
- 13 J. A. Rodríguez-Añón, F. Fraga López, J. Proupín Castiñeiras, J. Palacios Ledo and L. Núñez-Regueira, *Bioresource Technol.*, 52 (1995) 269.
- 14 A. Lehninger, *Bioquímica S. A.*, Omega, 2nd ed. pp. 618–623. Barcelona.