JOURNAL OF AGRICULTURAL ENGINEERING

RIVISTA DI INGEGNERIA AGRARIA

EDIZIONI ETS

VOL. XL - NO. 3 - SEPTEMBER 2009

CONTENTS

CALORIFIC VALUE DETERMINATION OF SOLID BIOMASS FUEL BY SIMPLIFIED METHOD

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1. Introduction

The whole process of thermal utilization of solid biofuels (fuel supply, combustion system, solid and gaseous emissions) is influenced by the kind of solid biofuel used, its physical characteristics (e.g. particle size, bulk density, moisture content, calorific value) and its chemical composition [Obernberger 2006]. These parameters are fundamental for the definition of the commercial value of the materials [Fernandez Llorente 2008], for the measurement and the evaluation of the plant efficiency, and the judgment of the technical-economic convenience of a process. For these purposes, the calorific value should represent the most important characteristic for the establishing the price of the solid biomass.

The parameter that is necessary for the definition of the energetic content of the materials is the gross calorific value (*GCV*) or high heating value. It represents the absolute value of the specific energy of combustion, in joules, for unit mass of a solid biofuel burned in oxygen in a calorimetric bomb under the conditions specified [CEN/TS 14918:2005]. On the basis of the *GCV* and the elemental composition, the net calorific value (*NCV*) is calculated. CEN/TS 14918 defines *NCV* at a constant pressure as the absolute value of the specific heat (enthalpy) of combustion, in joules, for unit mass of the biofuel burned in oxygen at constant pressure under such conditions that all the water of the reaction products remains as water vapour (at 0.1 MPa), the other products being as for the gross calorific value, all at the reference temperature. The *NCV* expresses the actual energetic content of combustible with respect to a precise humidity value.

The calculation of *GCV*, measured in a bomb calorimeter, is particularly important for the solid bio-

fuels since they generally have high variability in their chemical-physical composition. Nevertheless, in many applications it may not be easy to measure the *GCV*. The measurement is complicated and is a time-consuming process that requires set-up, measurement and calculation procedures.

In the absence of calorimetric data, the *GCV* of a solid biomass may be estimated by the element composition [Meraza 2002; Meraza 2003]. The conventional analysis, i.e. proximate and ultimate analyses (or elemental analysis), is a basic fuel characterization and can be carried out more easily, quickly, and cheaply by using common or modern laboratory equipments [Sheng 2005]. Numerous empirical equations have been published to relate the heating value of fuel to the its element composition of fuel as obtained by the element analysis [Meraza 2003; Gharagheiz 2008; Friedl 2005; Thipkhunthoda 2005; Demirbas 1997]. Nevertheless, fewer correlations have been developed on biomass. There are numerous correlations to calculate *GCV* from the element composition of fuel, most of which have been derived from coal [Parikha 2005; Channiwala 2002]. Many correlations derive from the Dulong correlation, exclusively based on the percentage content of hydrogen (*H*), carbon (*C*) and oxygen (*O*). Other elements that constitute solid biomass were considered in other correlations: nitrogen (*N*), sulphur (*S*) and ash content.

The correlations available in the literature are reported with high accuracy applied to the investigator's own database. An extrapolation to various biomass species, however, leads to considerable differences among the calculated results of the correlations. As a result, it would be very confusing for engineers to make their own selection [Sheng 2005]. It can be assumed that it is similar to the generalized extension of the correlation with various types of combustibles, including biomasses, available in literature, and that it does not envisage the different chemical complexity of the materials and its impact on the energetic content. For example, wooden materials have different cellulose, hemicelluloses and lignin compositions [Giordano 1971] while some biomasses can even contain variable fractions of fat.

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The *GCV* of a lignocelluloses fuel is a function of its lignin content. In general, the *GCV* of lignocelluloses fuels increases with the increase of their lignin contents and the *GCV* is highly correlated with lignin content. Again the heat content is affected by the proportion of combustible organic components (called extractives) present in it [Demirbas 2001].

A general evaluation of the correlations found in literature highlights how the accuracy of the correlations based on the proximate analysis data are very low since the analysis provides only the empirical composition of biomass [Sheng 2005]. The formulae based on the ultimate analysis are generally more accurate than those based on proximate analysis. The quality of the correlations based on chemical analysis was found to be very poor because of the variation of the biomass components properties as well as the biomass chemical composition. The regression coefficients of all the correlations, including the proposed ones, are less than 0.85. This shows the effect of variations in the biomass components [Meraza 2003]. Moreover, in various studies, it has been found that the data used to calculate the correlations were not measured directly by the author but deduced from other literature and other sources with a probable increase of errors.

At the Polytechnic University of the Marche Region, Ancona, there is a research lab on biomass for energetic use (Biomass Lab) which carries out various chemical-physical analyses on various types of materials. Given the high availability of analysis data, conducted with the same methods and tools, it has been considered useful to test the performance of some *GCV* measurement models defined in literature or deduced from the statistical analysis of available data. Additionally, aim of this study was the development of simplified model for the determination of *GCV* and *NCV* values through analytical correlations contained few parameters.

2. Material and methods

For this study the data from the analysis of 451 samples of biomasses of different types and origins was used. The chemical-physical analyses on materials were carried out according to the methodologies described in CEN technical normative for solid biomass. The data from the analysis are archived in a database to facilitate the organization of specific research and data processing.

The study procedure used on the biomass samples involves an initial preparation phase of the latter in compliance with CEN/TS 14780 and then specific physical-chemical analysis will be carried out on them. Within this study, the following parameters were recorded: ash content dry basis (A_C), gross calorific value dry basis (*GCV*) and the element composition (*C,H,N,S* and *O*). As for the *GCV* and the element analysis the value of the net calorific value on

dry basis *NCV* was calculated. Table 1 summarizes the methodologies used and the main summary information of the analytic parameters measured in this study. The analyzed samples are represented by lignin-cellulose type of materials of which 50% is made of pellets and chips, generally produced from waste from wood or forests and the remaining part from agriculture by-products (straw, fruit plan cuttings, waste from cultivation harvesting, etc.) or waste from agro-industrial processes (olive and grape cake, sunflower cake, husks, etc.).

For the data processing, the database was sub-divided into two distinct parts. The first part of the database, – database for calculations (DB_c) – made up of data from 200 samples, was used to calculate the correlations of the *GCV* measurement starting with the element composition and the ash content. On the remaining data – database for application (DB_a) – the models were tested on their performance. This criterion of management of the database allows to return a first evaluation on the forecast ability of the models. More in detail the measure of this ability is linked from parameters that measure the difference among the expected data from the model and the real data.

In every database, descriptive statistics were carried out to calculate the mean, the standard deviation (*SD*), the coefficient of variability (*CV*) and the maximum and minimum median for every parameter. The development of the models to calculate the *GCV* was conducted through the application of the regression analysis on the DB_c data. Statistical analysis has considered all the possible resultant models from the combination of all the variables. The best obtained correlations, chosen on the basis of the values of the R^2, were tested on the contents of the data in the DB_a. The same method was applied on the mathematical correlations identified in the bibliography and applied on solid biomasses. The latter are shown in Table 2, in which *C, H, N, O* and *S* represent the percentage content on dry basis of carbon, hydrogen, nitrogen, oxygen and sulphur respectively. All the statistical analysis of this work was conducted with the software MINITAB® Release 14. The criteria used to evaluate the performance of the various correlations was based on the calculation of the average absolute error (*AAE*) and average bias error (*ABE*) computed as follows [Friedl 2005; Demirbas 1997]:

$$AAE = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{GCV_c - GCV_m}{GCV_m} \right| \cdot 100 \qquad (1)$$

$$ABE = \frac{1}{n} \sum_{i=1}^{n} \left(\frac{GCV_c - GCV_m}{GCV_m} \right) \cdot 100 \qquad (2)$$

in which GCV_c is the calculated gross calorific value dry basis while GCV_m is the measured gross calorific value dry basis and *n* is the number of all samples. The mathematical correlations marked by absolute values that are lower than *AAE* and *ABE*

Analysis	Normative	Apparatus	Precision
A_c	CEN/TS 14775	Electric muffle furnace	$\pm 0.1\%$
GCV	CEN/TS 14918	Isoperibolic bomb calorimeter – IKA 2000	± 4.18 kJ
NCV	CEN/TS 14918	Method of measurement	± 4.18 kJ
Element analysis	CEN/TS 15104	Perkin Elmer – Calculation of percentage content of C, H, N, O, S	$\pm 0.03\%$

TABLE 1 - Technical normative considered for the execution of analysis.

Number	Model	Author	Unit
1	$GCV = 1.87C^2 - 1.44C - 2820H + 63.8C \cdot H + 129N + 20147$	Friedl, 2005	kJ/kg
2	$GCV = 5.22C^2 - 319C - 1647H + 38.6C \cdot H + 133N + 21028$	Friedl, 2005	kJ/kg
3	$GCV = 3.55C^2 - 232C - 2230H + 51.2C \cdot H + 131N + 20600$	Friedl, 2005	kJ/kg
4	$GCV = 491.2C - 911H + 117.7O$	Thipkhunthod, 2005	MJ/kg
5	$GCV = 430.2C - 186.7H - 127.4N + 178.6S + 184.2O - 2379.9$	Thipkhunthod, 2005	MJ/kg
6	$GCV = -1.3675 + 0.3137C + 0.7009H + 0.0318 O$	Sheng, 2005	MJ/kg

TABLE 2 - Models chosen from literature (all the parameters are on dry basis).

were considered to be the most suitable for the calculation of GCV.

An important part of the research has been devoted to the development of a mathematical relationship for the simplified determination of the NCV through the measure of C. On the base of (3) it is possible to calculate NCV beginning from GCV and from the knowledge of the element composition [CEN/TS 14918:2005].

$$NCV = GCV - 212.2\,H - 0.8\,(O + N) \qquad (3)$$

If such equation is applied to a typical composition of lignocellulosic biomass ($H = 6\%$; $O = 39\%$ e $S = 0,1\%$) it is observed that H influence more than other two elements. It is possible to deduct how the energetic contribution of hydrogen, when calculating NCV, has a weight of over 30 times greater than that from the other two elements. Additionally the existence of a bond between H and C is presumable. In this way C, when implemented in mathematical models, it could be considered representative of H.

In particular, on this aspect an analysis of the distribution of the relationship has been conducted among C and H (C/H) for the different material considered in DB_c dividing them in classes of origin (Table 3). With the purpose to underline some differences among the various groups of materials an analysis ANOVA one-way, test di Tukey 95%, it has been conducted.

Similar to GCV, for NCV the criteria used for the evaluation of the correlation performance is based on the calculation of AAE (4) and ABE (5). In particular:

$$AAE = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{NCV_c - NCV_m}{NCV_m}\right| \cdot 100 \qquad (4)$$

$$ABE = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{NCV_c - NCV_m}{NCV_m}\right) \cdot 100 \qquad (5)$$

in which NCV_c is the calculated net calorific value dry basis while NCV_m is the net calorific value dry basis measured with the appropriate method and n is the number of all samples.

3. Results

Tables 4 and 5 include the main descriptive statistical parameters of the two databases used for this study.

On the whole, the characteristics of the samples from the two databases are very similar, especially for the value of GCV and of C and H. Some differences were only registered for the A_c and N values. Table 6 contains the results of the regression analysis developed on DB_c. The mathematical correlations obtained and the relative R^2 values are given in detail. It can be noticed that all the correlations present R^2 values between 0.7 and 0.8, higher even if to a small extent, for the more variable correlations. It is possible to note that the simple correlation, equation 10, that links the

Biomass class	Samples (n)
Forestal	84
Arboreous	7
Agro-industrial	34
Herbaceous	17
Nuts	16
Faecal matter	7
Seeds and oilcake	35

TABLE 3 - Composition of the DB_c according to the classes of origin.

GCV only to *C*, presents R^2 value that is a little lower than that of more complex correlations, i.e. equation 9 and 11, containing 5 and 4 variables, respectively to be used for in the calculation. The performance test of the correlations recorded in Table 2 and Table 6, applied to 251 data from the DB_a, is represented by the *AAE* and *ABE* values reported in Table 7. Except for equations 5 and 6, the results show *AAE* values of less than 3.3% and *ABE* values between -1.95% and 0.85%. The general observation is that, on average, the equations underestimate the *GCV* value compared to the real one.

Element	Unit	Average	SD	CV	Min	Median	Max
C	%	48.4	4.4	9.0	23.6	49.2	60.2
H	%	6.1	0.5	8.2	2.7	6.1	7.6
N	%	1.2	1.5	116.3	0.0	0.7	8.0
O	%	38.8	6.6	17.0	9.9	41.1	46.2
S	%	0.1	0.2	171.3	0.0	<0.1	1.0
A_c	%	5.3	8.4	159.4	0.1	1.9	49.7
GCV	kJ/kg	19134	2064	10.8	10800	19205	27330

TABLE 4 - Descriptive statistic of DB_c.

Element	Unit	Average	SD	CV	Min	Median	Max
C	%	47.7	3.3	7.0	24.3	48.4	52.3
H	%	6.2	0.6	10.6	3.3	6.3	8.8
N	%	0.8	0.6	81.5	0.2	0.6	4.7
O	%	39.4	4.4	11.3	17.6	40.3	63.2
S	%	0.1	<0.1	121.2	0.0	<0.1	0.5
A_c	%	6.1	5.0	81.8	0.3	4.4	28.3
GCV	kJ/kg	18946	1193	6.3	13065	19247	23015

TABLE 5 - Descriptive statistic of DB_a.

Among the relations taken from bibliography, equation 2 shows better *AAE* and *ABE* values, 2.66% and -0.20% respectively. Similar results were obtained with equation 10 that seems to be the best among those found from the data of this study. In the graph of Figure. 1 there are the values of *C* with respect to *H*. Indeed it shows the presence of a positive relationship between the two elements though with a

Equation	ABE	AAE	Reference
	(%)	(%)	
1	0.69	2.73	Friedl, 2005
2	-0.20	2.66	Friedl, 2005
3	-0.62	3.12	Friedl, 2005
4	0.79	2.75	Thipkhunthod, 2005
5	18.99	19.09	Thipkhunthod, 2005
6	27.65	27.65	Sheng, 2005
7	0.85	3.27	Current author
8	-0.89	2.94	Current author
9	-1.95	3.06	Current author
10	-0.27	2.80	Current author
11	-1.93	3.05	Current author

TABLE 7 - *ABE* and *AAE* values relative to the various empirical correlations for the calculation of *GCV*.

low correlation that has R^2 of 0.49. Anyway, the biomasses with high C potentially contains in average a greater value of H.

When considering a typical composition of lignocelluloses biomass with carbon content between 45% and 55%, an average *C/H* value between 7.2 and 8.1 is observed (Table 8).

Nevertheless, the analysis of the *C/H* value for the various biomass classes, as defined in Table 3, shows some differences. Table 8 contains the average values of *C/H* for every biomass.
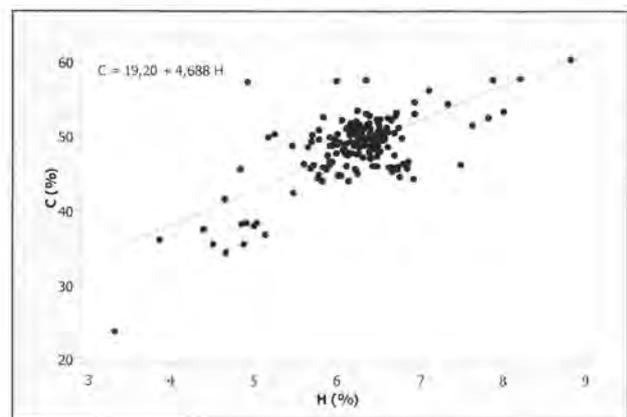

Fig. 1 - Relationship between *C* and *H* for different samples.

Number	Typology	R^2	Unit
7	$GCV = 971 + 323,6C + 711H$	0.754	kJ/kg
8	$GCV = -2494 + 379,3C + 468,8H + 292,6N$	0.772	kJ/kg
9	$GCV = -4311 + 401,1C + 294,3H + 340,7N + 42,3O + 298S$	0.783	kJ/kg
10	$GCV = 297,6 + 389,7C$	0.728	kJ/kg
11	$GCV = -79,5 + 358,7C + 252H + 298,5N + 1201S - 177,1A_c$	0.783	kJ/kg

TABLE 6 - List of correlations tested for the development of model and R^2 value.

Biomass	C/H	
	Average	SD
Forestal	7.93	0.48
Arboreous	7.67	0.25
Agro-industrial	7.85	0.49
Herbaceous	8.40	0.88
Nuts	8.24	1.35
Animal dejections	7.31	0.22
Seeds and oilcake	7.19	0.65

TABLE 8 - Average values and SD of functioning C/H for the various biomass classes.

It is interesting to observe the differences of the C/H value in various groups of the biomass class. Specifically, the arboreous, forest and the agro-industrial classes have an intermediate C/H value between 7.7 and 7.9 (group A), unlike the herbaceous and nut classes with a C/H value of 8.2 and 8.4 (group B). Then follows a third group of products made up of animal dejections, seeds and oilcake for extraction (group C) with average C/H values between 7.2 and 7.3.

Results from ANOVA one-way test (Table 9), have put in evidence significant difference among the three groups (p<0,001 and F statistic = 18,28). Finally, the graph of Figure 2 shows the relation that links the NCV with the C.

The correlation that has R^2 value of 0.715, has shown high performance in the test with the DB_a with ABE and AAE values of 0.28% and 3.99%, respectively.

Tukey contrast	Difference	95% CI	Note
C vs A	-0.430	- 0.811 to - 0.048	Significant
C vs B	0.683	0.336 to 1.026	Significant
A vs B	1.111	0.657 to 1.563	Significant

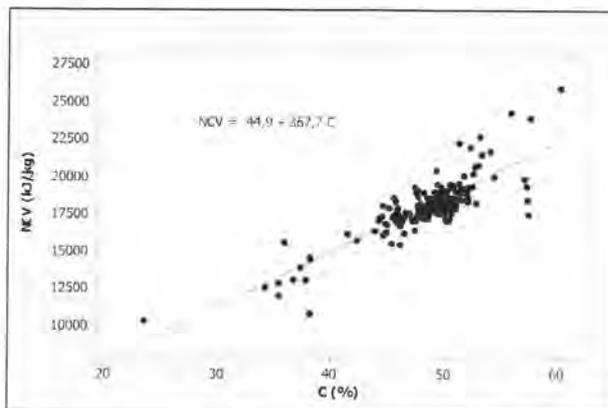TABLE 9 - Results from ANOVA one-way applied on different biomasses groups.

Fig. 2 - Correlation between NCV and C.

4. Considerations

A simple and economic calculation of the energetic content of the biomasses can be affected by using the specific mathematical correlations that link GCV with the basic composition. The correlations tested in this work highlight how this objective can be reached with ABE and AAE, lower than the absolute 2.0% and 3.2%, respectively. For generic biomasses, such as those analyzed by the author, there will be average errors lower than 630 kJ/kg which will go down to less than 500 kJ/kg for the most performing mathematical correlations. The latter data is about 4 times the limit of repeatability provided for in CEN/TS 14918 – "Solid Biofuels – Method for the determination of calorific value" and corresponds to the effect that it will have on the estimation of the energetic content of the biomass, deriving from an error on the humidity content between about 2% and 3% included. Such result appears important in relationship to the aim proposed regarding the simplified determination of the GCV.

Nevertheless, not all the correlations present in literature, even if marked by good statistical parameters (equations 5 and 6), can produce satisfying estimations. It is possible to hypothesize how this type of biomass, originating from the data on which these models were developed, presents various characteristics producing mathematical relations which does describe the behaviour of the various material well. The importance of the errors of measurement must also be added. It is significant in the case of mathematical correlations produced with data from bibliographical sources (sometimes different) and not from measurements obtained with standard analytic methods. Both the calculation of GCV with calorimetric cylinder and that of the element composition, involve weighing for the biomass quantity with high precision and the continuous calibration of the tools that can condition the quality of the data.

The study also shows that the simple correlations have performances that can be compared with those of more complex ones. Among these, correlation 10 which links GCV to the only carbon content, which has shown an AAE value of about 2.8%. The observation that the carbon content is partly representative of the hydrogen content, which affects the NCV calculation in a preponderant manner, could justify the good correlation that it has with the latter parameter. This correlation, whose AAE was found to be less than 4%, calculated on real NCV data, can be an important possibility for the simplification of material analysis, above all in those operative contexts, like a power plant, in which the monitoring of the energetic content of the biomass is intense. The improvement of these models and the predisposition of the carbon and humidity analyzers operating continuously or semi-continuously on conveyor belts may open the possibility to develop systems for the calculation of the biomass energetic content in big energetic plants al-

lowing more frequent monitoring in shorter time with consequent benefits in economic terms and reduction analysis time.

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SUMMARY

The gross calorific value (GCV) and, in particular, the net calorific value (NCV) are fundamental physical parameters in the use of energetic biomass. The method of measurement and the calculation of the GCV, defined by CEN/TS 14918, is rather complex and, in many cases, has a time and cost importance. In literature there are some studies in which the empirical correlations between GCV and the element composition have been calculated. In these contribution some of the most significant correlations in literature are tested and compared to others obtained from statistical processing of data from analysis on 200 samples of biomass carried out in the laboratory and with standard CEN methods. The study shows how the very simplified correlations based on the calculation of carbon and hydrogen content have performances that are similar to those of more complex ones based on the greater number of parameters. In particular, the empirical correlation ($GCV = 297.6 + 389.7C$) produced from this work has errors that are comparable to those of the better correlation highlighted by literature ($GCV = 5.22C^2 - 319C - 1647H + 38.6C \cdot H + 133N + 21028$).

Keywords: calorific value, estimating, solid biomass, elemental analysis, fuel.

List of symbols

AAE	average absolute error (%)
ABE	average bias error (%)
A_C	ash content (%)
C	carbon content (%)
C/H	ratio carbon hydrogen
CV	variability coefficient (%)
DB_a	database for application
DB_c	database for calculation
GCV	gross calorific value (kJ/kg)
H	hydrogen content (%)
N	nitrogen content (%)
NCV	net calorific value (kJ/kg)
O	oxygen content (%)
S	sulfur content (%)
SD	standard deviation