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Solid biofuels — Conversion of analytical results from one basis to another



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National foreword

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Solid biofuels - Conversion of analytical results from one basis to another

Biocombustibles solides - Conversion de résultats analytiques d'une base en une autre base

Feste Biobrennstoffe - Umwandlung von Analysenergebnissen einer Bezugsbasis in Ergebnisse mit anderer Bezugsbasis

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Cont	Pa	ge
Forew	ord	3
Introdu	uction	4
1	Scope	5
2	Normative references	5
3	Symbols	5
4	Principle	6
5	Calculations for analyses of solid biofuels	6
5.1	General	_
5.2 5.2.1	Extra calculations for hydrogen, oxygen and net calorific value	
5.2.2	Oxygen	
5.2.3	Net calorific value	
5.3	General equations for the conversion from one basis to another basis	
Annex	A (informative) Tools for integrity check	8
A .1	General	
A.2	Integrity check based on the carbon results	
A .3	Integrity check based on the major elements and the ash results	
A.4	Integrity check based on the C H N O and ash results	9
Annex	B (informative) Tables with units and conversion factors	11
Annex	C (informative) Guideline for the use of validation parameters	12
Bibliog	graphy	14

Foreword

This document (EN 15296:2011) has been prepared by Technical Committee CEN/TC 335 "Solid biofuels", the secretariat of which is held by SIS.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by August 2011, and conflicting national standards shall be withdrawn at the latest by August 2011.

This document supersedes CEN/TS 15296:2006.

In the pre-normative project BIONORM I&II a robustness test has been performed to find out if all critical parameters in the standard were addressed. Based on the results of that test it has been concluded that all critical parameters were covered. Only minor technical changes were necessary which have been implemented in the revised text. The revision also includes a change of deliverable from Technical Specification to European Standard and updated normative references.

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Introduction

In the CEN Standards covering the analysis of solid biofuels it is generally specified that the determination should be carried out on the air-dried or in air equilibrated general analysis test sample, prepared according to FprEN 14780 [1]. However, in making use of these analyses, it is necessary to express the results on dry basis and sometimes also on some other basis. The bases in common use for solid biofuels are "air-dried" (sometimes stated as "as determined"), "as received" (sometimes stated "as sampled" or "as delivered"), "dry" and "dry, ash free".

1 Scope

This European Standard gives equations, which allow analytical data relating to solid biofuels to be expressed on the different bases in common use. Consideration is given to corrections that may be applied to certain determined values for solid biofuels prior to their calculation to other bases.

In the informative Annex A tools for integrity checks of analytical results are given. In the informative Annex B conversion factors for calculation into other units are given. The informative Annex C is a guideline for the use of validation parameters as can be found in analytical standards of CEN/TC 335.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 14774 (all parts), Solid biofuels — Determination of moisture content — Oven dry method

EN 14775, Solid biofuels — Determination of ash content

EN 14918, Solid biofuels — Determination of calorific value

EN 14961-1, Solid biofuels — Fuel specifications and classes — Part 1: General requirements

EN 15104:2011, Solid biofuels — Determination of total content of carbon, hydrogen and nitrogen — Instrumental methods

EN 15289, Solid biofuels — Determination of total content of sulfur and chlorine

3 Symbols

The symbols employed in the subsequent clauses are as follows, with the indices "ad" (air-dried), "ar" (as received), "d" (dry), "daf" (dry, ash free) where appropriate:

- A ash (percentage by mass) according to EN 14775;
- C total carbon content (percentage by mass) according to EN 15104;
- C/ total chlorine content (percentage by mass) according to EN 15289;
- $q_{p,net}$ net calorific value at constant pressure (J/g) according to EN 14918 or (MJ/kg) according to EN 14961-1;
- H total hydrogen content (percentage by mass) according to EN 15104;
- M moisture content (percentage by mass) according to EN 14774 (all parts);
- N total nitrogen content (percentage by mass) according to EN 15104;
- O total oxygen content (percentage by mass);
- S total sulfur content (percentage by mass) according to EN 15289.

4 Principle

In order to convert an analytical result expressed as one basis to another basis, it is multiplied by a factor calculated from the appropriate equations (see Table 1) after insertion of the requisite numerical values into the equations in question.

5 Calculations for analyses of solid biofuels

5.1 General

Most analytical values on a particular basis may be converted to any other basis by multiplying it by a factor calculated from the appropriate equation given in Table 1, after insertion of the requisite numerical values into the equation in question. However, for some parameters there is a direct involvement of the moisture content. In these cases a correction as specified in 5.2 of the air-dried result shall be carried out before calculation to dry basis or dry, ash free basis. Also, if a result for these parameters expressed on a dry or a dry, ash free basis is to be recalculated to a moist basis, the corrections stated in 5.2 shall be added back to the actual moist basis after applying the appropriate equation from the table.

5.2 Extra calculations for hydrogen, oxygen and net calorific value

5.2.1 Hydrogen

The hydrogen content determined on the air-dried basis (H_{ad} , as analysed) includes both the hydrogen content of the combustible part of the solid biofuel as well as the hydrogen present in the sample as moisture (total hydrogen content). Before calculation to any other basis the determined hydrogen content, H_{ad} , shall be corrected of the moisture bound hydrogen by calculation to dry basis, H_{d} :

$$H_{\rm d} = (H_{\rm ad} - M_{\rm ad} / 8,937) \times \frac{100}{(100 - M_{\rm ad})}$$
 (1)

This hydrogen content, related to the combustible part of the solid biofuel, may be converted to any other basis using the equations in Table 1.

5.2.2 Oxygen

The oxygen content related to the combustible part of the solid biofuel can be calculated by difference on the dry basis using the equation:

$$O_{d} = 100 - C_{d} - H_{d} - N_{d} - S_{d} - CI_{d} - A_{d}$$
 (2)

NOTE If high precision is required, the values of S_d and Cl_d should be corrected for eventual remaining contents of sulfur and chlorine in the ash (A_d) .

5.2.3 Net calorific value

The net calorific value at constant pressure on a moist basis ($q_{\rm p,net,M}$) includes a correction for the heat of vaporization concerning the actual moisture content, M (M being e.g. $M_{\rm ad}$ or $M_{\rm ar}$). Before conversion to any other basis, using the equations in Table 1, this correction corresponding to 24,43 J/g per weight percent moisture (24,43 x M) shall be undone by adding 24,43 x M to the value of the net calorific value. After multiplying this sum with the appropriate equation from Table 1, the obtained value then is to be corrected for the heat of vaporization concerning the new moisture content, M^* , by subtracting the value 24,43 x M^* . These corrections are illustrated in Equation (3) concerning the conversion of the net calorific value for a moisture content M to the net calorific value for a moisture content M^* , both at constant pressure and in J/g:

$$q_{\text{p,net,M*}} = \left[q_{\text{p,net,M}} + (24,43xM)\right] x \frac{100 - M^*}{100 - M} - (24,43xM^*)$$
(3)

For the conversion of e.g. the net calorific value on dry basis $(q_{p,net,d} \text{ in J/g})$ to the net calorific value on as received basis $(q_{p,net,ar} \text{ in J/g})$, Equation (3) can be simplified into:

$$q_{\rm p,net,ar} = q_{\rm p,net,d} \times \frac{100 - M_{\rm ar}}{100} - 24{,}43 \times M_{\rm ar}$$
 (4)

as in this case, M = 0 and $M^* = M_{ar}$

The net calorific value at a constant pressure for a dry sample $(q_{p,net,d})$ is derived from the corresponding gross calorific value at a constant volume according to EN 14918.

5.3 General equations for the conversion from one basis to another basis

After applying eventual corrections according to 5.2, analytical values on a particular basis may be converted to any other basis by multiplying it by a factor calculated from the appropriate equation given in Table 1, after insertion of the requisite numerical values into the equation in question.

Table 1 — Equations for calculating conversion factors to convert analytical results from one basis to another

Given		Wante	d	
	As analysed	As received ^a	Dry	Dry, ash free
	(air dried)			
	(ad)	(ar)	(d)	(daf)
As analysed		$\frac{100 - M_{\rm ar}}{100 - M_{\rm ad}}$	$\frac{100}{100 - M_{ad}}$	$\frac{100}{100 - (M_{\rm ad} + A_{\rm ad})}$
(air dried, ad)				
As received	$\frac{100 - M_{ad}}{100 - M_{ar}}$		$\frac{100}{100 - M_{\rm ar}}$	$\frac{100}{100 - (M_{\rm ar} + A_{\rm ar})}$
(ar)				
Dry (d)	$\frac{100 - M_{ad}}{100}$	$\frac{100 - M_{ar}}{100}$		100 100 – A _d
Dry, ash free	$\frac{100 - (M_{\rm ad} + A_{\rm ad})}{100}$	$\frac{100 - (M_{\rm ar} + A_{\rm ar})}{100}$	$\frac{100 - A_d}{100}$	
(daf)				

^a Note that the equations given for calculating results to the "as received" basis may be used to calculate them to any other moisture bases.

Annex A (informative)

Tools for integrity check

A.1 General

In this annex, three integrity checks are described. It will help users to evaluate analysis results; these tools will be especially useful when larger series of results have to be checked on analysis/typing errors.

A.2 Integrity check based on the carbon results

Calculate the estimate, QB, for the net calorific value at constant pressure on dry basis from the carbon content, using Equation (A.1):

QB (in MJ/kg) =
$$0.274 6 \times C_d + 5.79$$
 (A.1)

Compare this calculated QB value with the measured value $q_{p,net,d}$ in MJ/kg.

A.3 Integrity check based on the major elements and the ash results

Add the results of the major elements after conversion to their composition on oxide basis. The sum of these oxides (Mash) can then be compared to the ash content (550 $^{\circ}$ C). For samples with a high S and or Cl content these values should be added as well. The conversion factor for S is 2,50; for Cl the conversion factor is 1.

The conversion factors for converting the major elements into their oxide forms are:

 $AI \rightarrow AI_2O_3$: 1,89

Ca \rightarrow CaO : 1,40 Fe \rightarrow Fe₂O₃ : 1,43

Mg → MgO : 1,66

 $P \rightarrow P_2 O_5 : 2,29$

 $K \rightarrow K_2O$: 1,20 $Si \rightarrow SiO_2$: 2,14

Na \rightarrow Na₂O : 1,35 Ti \rightarrow TiO₂ : 1,67

Calculate the sum Mash in % m/m on dry basis according to Equation (A.2) using the element concentrations in mg/kg on dry basis.

$$\begin{aligned} \text{Mash} &= (\text{AI}_d \times 1,89 + \text{Ca}_d \times 1,40 + \text{Fe}_d \times 1,43 + \text{Mg}_d \times 1,66 + \text{P}_d \times 2,29 + \text{K}_d \times 1,20 + \text{Si}_d \times 2,14 + \text{Na}_d \times 1,35 + \text{Ti}_d \times 1,67 + \text{CI}_d + \text{S}_d \times 2,50) \, / \, \, 10 \,\, 000 \end{aligned} \tag{A.2}$$

The ratio Mash / ash should be around 1 (0,8 to 1,2).

NOTE 1 If the sum of the oxides is less than the ash content, the explanation may be a high content of carbonates.

NOTE 2 With high S and/or CI content, be aware that more than 50 % of these elements could be lost by ashing at $550 \,^{\circ}$ C.

A.4 Integrity check based on the C H N O and ash results

This check is only possible if the O content has been determined.

Calculate the sum MB according to Equation (A.3):

$$MB = C_d + H_d + N_d + O_d + S_d + CI_d + A_d$$
 (A.3)

(All values in %)

The MB value should be around 100.

NOTE In some types of solid biofuels relative high amounts of F, Br or I are found. In that case the contribution of these elements shall be accounted for as well.

Table A.1 — Examples of the integrity checks according to A.1, A.2 and A.3

Element	С	Н	N	0	Al	Ca	Fe	K	Na	Mg	Si	D	Ti	S	CI	Ash	<i>a</i>	MB	Mas h	QB
Element		- 11	IN	0	Al	Ca	16	I N	iva	ivig	SI	Г	11	3	CI	ASII	$q_{ m p,net,d}$	IVID	- 11	MJ/k
Unit	%	%	%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	MJ/kg	%	%	g
Wood+bark	46,4	6,20	0,01	42,5	44	1 398	46	637	25	175	236	65	3	75	11	0,6	19,2	96	0,4	18,5
Straw	44,4	5,86	0,65	43,7	71	2 829	87	10 770	70	754	11 130	706	25	1 008	1 112	5,6	17,9	100	4,8	18,0
Bark	46,5	5,38	0,56	41,4	536	45 290	297	2 080	115	531	3 175	196	41	741	40	13,3	16,5	107	7,8	18,6
Rapestraw	44,8	5,69	0,34	44,7	34	11 100	25	8 970	653	567	194	551	2	1 943	2 814	4,8	17,7	100	3,9	18,1
Thistle	43,0	5,73	1,03	41,8	411	13 380	238	13 130	12 310	2 308	1 074	795	10	2 002	17 280	9,9	16,8	101	8,3	17,6
Fir without bark	47,8	6,10	0,05	43,9	51	784	15	311	3	103	25	23	3	41	3	0,3	19,2	98	0,2	18,9
Exhausted																				
olive residue	46,0	5,45	1,37	38,7	2 214	13 860	1 512	23 870	166	2 955	10 060	1 47 4	133	1 336	2 074	11,5	19,3	103	9,1	18,4
Wood with glue	50,7	5,78	0,25	42,9	39	4 180	52	944	83	484	80	6	4	167	89	1,5	20,5	101	0,9	19,7
Seaweed	32,3	4,20	2,49	36,1	11 250	19 230	4 440	9 885	11 505	7 620	74 880	1 43	321	20 525	1 847	31,5	12,8	107	32,2	14,6
Coconut shells	49,2	5,54	0,22	45,0	263	697	164	3 410	1 900	575	1 785	128	12	380	1 788	2,1	19,6	102	1,6	19,3
Almond kernels	49,1	6,17	0,22	47,3	108	2 765	237	4 165	49	313	2 430	199	14	177	93	1,9	19,5	105	1,6	19,3
Palm pit kernels	50,8	5,87	0,32	42,8	619	5 460	487	1 240	92	517	8 010	272	31	310	149	3,1	20,2	103	3,1	19,7

All results are on dry basis where:

MB are the calculated values according to A.4;

Mash are the calculated values according to A.3;

QB are the calculated values according to A.2.

Annex B (informative)

Tables with units and conversion factors

Table B.1 — Conversion factors 1

	toe	MWh	GJ	Gcal
toe	1	11,63	41,868	10,0
MWh	0,085 98	1	3,600	0,859 8
GJ	0,023 88	0,277 8	1	0,238 8
Gcal	0,1	1,163 0	4,186 8	1

For example: 1 toe = 11,63 MWh

Table B.2 — Conversion factors 2

To convert from:	То:	Multiply by:
g/cm ³	lb/ft ³	62,427 974
lb/ft ³	kg/m ³	16,018 46
lb/in ³	kg/m ³	27 679,90
lb/ft ³	g/cm ³	0,016 018 46
cm	mil	393,70
joule (J)	вти	9,484 5 ·10 ⁻⁴
вти	joule (J)	1 054,350

toe = tonne oil equivalent

A thou, also known as a "mil" or "point", is a measurement unit of length equal to 0,001 inch (a "milli-inch", one thousandth of an inch).

Annex C (informative)

Guideline for the use of validation parameters

A laboratory has to prove the accuracy of a method in its own laboratory, e.g. either by using Certified Reference Materials (CRMs) or by participation in round robins. When comparing obtained results with validation data presented in the CEN analytical standards, it has to be taken into account that the concentration of a component might vary over orders of magnitudes in different biomass samples. When measuring close to the detection limits of instruments for elements in very low concentrations, standard deviation and errors usually increase. Furthermore some solid biofuels are difficult to homogenize or contain impurities and the sample homogeneity as well as the biomass type may influence the performance of the method.

Validation data may include the parameters listed in Table C.1.

Table C.1 — Validation parameters

Symbol	Meaning
n	is the number of laboratories after outlier elimination
l	is the number of outlier free individual analytical values
0	is the percentage of outlying values from replicate determination
X	is the overall mean
s_{R}	is the reproducibility standard deviation
CV_{R}	is the coefficient of the variation of the reproducibility
S_{Γ}	is the repeatability standard deviation
CV_{r}	is the coefficient of the variation of the repeatability
r	is the repeatability limit
R	is the reproducibility limit

If the r and R values are not included in presented validation data, they can be calculated from the standard deviations as follows:

 $r = 2\sqrt{2} \cdot s_r = 2.8 s_r$ (absolute comparison of 2 measurements at repeatability conditions)

 $r = 2\sqrt{2} \cdot CV_r = 2.8 \ CV_r$ (relatively comparison of 2 measurements at repeatability conditions)

 $R = 2\sqrt{2} \cdot s_R = 2.8 s_R$ (absolute comparison of 2 measurements at reproducibility conditions)

 $R = 2\sqrt{2 \cdot CV_R} = 2.8 \ CV_R$ (relatively comparison of 2 measurements at reproducibility conditions)

Available performance/validation data for a method, as can be found in CEN analytical standards, or the data from other reliable round robin investigations of the method may be used as one of the sources when determining the expanded uncertainty of measurement.

In that case it should be assured that:

- the method used by the laboratory performs as good or better than the performance data given in the standards. Usually, common quality assurance methods for laboratories such as control cards, use of CRM's, proficiency test or round robins, are necessary to document this;
- the types of samples analyzed are within the scope of the samples for which the data are valid (e.g. the type of samples investigated in the performed round robin);
- the analysis method included by the budget is the same method for which the data are valid (e.g. the method used by the participants in the performed round robin).

EXAMPLE 1 Use of validation data for the estimation of expanded uncertainty of measurement

A laboratory wants to determine the expanded uncertainty of measurement of their carbon determination in wood, and wants to include general accepted method specific data as part of that uncertainty budget.

The intralab reproducibility of this laboratory, calculated from internal validation studies and control charts, was determined to be 0,82% (CV_R).

The performance data presented in EN 15104:2011, Table A.1 state a CV_R (between laboratories) at 1,1 % relative (wood chip sample).

Then:

$$u_{\text{c,rel}} = \sqrt{(0.82^2 + 1.1^2)} = 1.37 \% \text{ relative}$$

$$U_{\text{rel}} = 2 \times u_{\text{c.rel}} = 2.7 \%$$
 relative

where

 $u_{\rm c.rel}$ is the combined uncertainty of measurement;

 $U_{\rm rel}$ is the expanded uncertainty of measurement using a coverage factor of 2 (\sim 95 % confidence interval).

EXAMPLE 2 Use of validation data for evaluation of double determinations

Available performance/validation data for a method may also be used for a control of the actual level of precision for the method, e.g. according to the following example.

In EN 15290:2011 [2], Table B.5, the following performance data is presented for the determination of phosphorous:

Table C.2 — Examples validation parameters

Sample	N	l	0	x	SR	CV_{R}	Sr	CV_{r}
			%	mg/kg	mg/kg	%	mg/kg	%
wood chips	11	53	3,6	74	5	6,7	2	3,4
exhausted olive residues	13	65	0	1 490	127	8,5	58	3,9

When analysing a sample of solid biofuel two results for the phosphorus content were obtained, 810 mg P/kg and 1 180 mg P/kg. The difference between these two results is 370 mg P/kg or 37 % of the mean value, 995 mg P/kg. At this level the repeatability limit (r) as calculated from the performance data presented in EN 15290:2011 [2] $(r = 2.8 \times CV_r)$ is expected to be 10 % to 11 % of the mean value. As the actual difference exceeds this interval significant, the results should not be accepted and the determination should be repeated after a survey of the procedure.

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