
Solid biofuels — Determination of ash melting behaviour

*Biocombustibles solides — Méthode de détermination de la fusibilité
des cendres*

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 238, *Solid biofuels*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The test method described in this document provides information about fusion and melting behaviour of the composite inorganic constituents of the solid biofuel ash at high temperatures.

Ash melting is a complex process where also sintering, shrinkage and expansion or swelling can occur.

The test method is empirical. The ash used for the test is a homogeneous material, prepared from the fuel by ashing at 550 °C (alternatively, ashing temperatures of 710 °C or 815 °C may be used). The determination is performed at a controlled rate of heating in a controlled atmosphere. In contrast, under full-scale conditions, the complex processes of combustion and fusion involve heterogeneous mixtures of particles, variable heating rates and gas compositions.

The determined characteristic temperatures in the test can be used for comparison of the tendency of the ashes from different types and qualities of solid biofuels to form fused deposits or to cause bed agglomeration on heating.

The method is based on the methods described in DIN 51730:1998^[1], ISO 540:2008^[2] and CEN/TS 15370-1^[3]. The terms ash fusibility and ash softening are synonyms to ash melting.

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1 Scope

This document specifies a method for the determination of the characteristic temperatures for the ash melting behaviour of solid biofuels.

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.

ISO 16559, *Solid biofuels — Terminology, definitions and descriptions*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 16559 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <http://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

3.1

shrinkage starting temperature

SST

temperature is defined as when the area of the test piece falls below 95 % of the original test piece area at 550 °C (or other ashing temperature used) due to shrinking of the test piece

Note 1 to entry: Shrinkage may be due to liberation of carbon dioxide and volatile alkali compounds. It may also be due to sintering and may be a first sign of partial melting.

3.2

deformation temperature

DT

temperature at which the first signs of melting occur

Note 1 to entry: It is common that DT will occur shortly before HT/FT. If the test results show a small temperature difference between SST and DT and a large temperature gap between DT and HT/FT it is advised that the analyst review the images to verify if the temperature recorded as DT is truly due to melting or if it is a shape change caused by excessive shrinkage.

Note 2 to entry: Deformation temperature can be seen as rounding of the edges, smoothing of surfaces, expansion of the cylinder or general changing of the cylinder shape. If the test piece starts to swell or bubble without the edges being rounded, the temperature is registered as DT (since swelling and bubbling only occur when a fraction of the ash is melted).

Note 3 to entry: For computerized evaluation a shape factor change can be used to define the deformation temperature. For definition of shape factor see [Annex A](#).

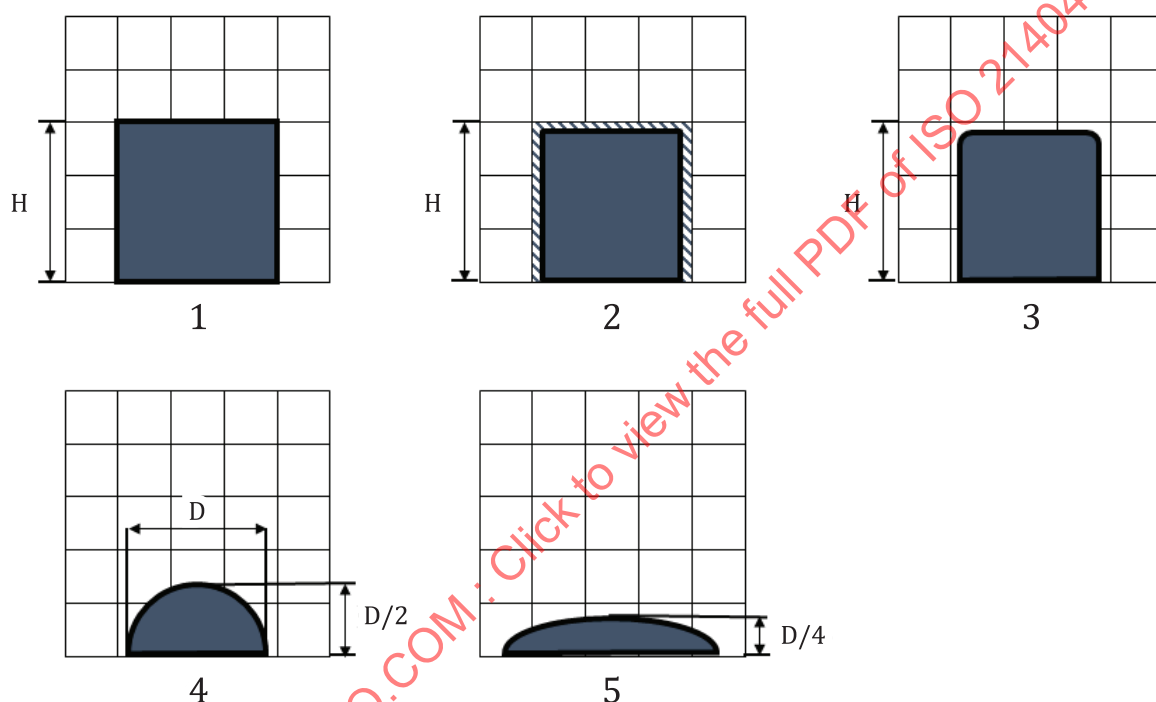
3.3 hemisphere temperature

HT
temperature at which the test piece forms approximately a hemisphere i.e. when the height is half of the base diameter

3.4 flow temperature

FT
temperature at which the ash is spread out over the supporting tile in a layer, the height of which is half of the height of the test piece at the hemisphere temperature as depicted in [Figure 1](#).

Note 1 to entry: Half of the height of the test piece at the hemisphere temperature has been defined due to frequently occurring bubbling effects. This is especially important for automatic image evaluation.



Key

- 1 original shape at reference (ashing) temperature
- 2 SST, Shrinkage starting temperature
- 3 DT, Deformation temperature
- 4 HT, Hemisphere temperature
- 5 FT, Flow temperature

Figure 1 — Phases which can occur in the ash melting process

4 Principle

Ash from biofuel is prepared under controlled conditions of time and equipment specifications to a controlled temperature of $(550 \pm 10) ^\circ\text{C}$. This ash is homogenized, and a test piece is made from the prepared ash. It is heated up at constant rate and is continuously observed while heated up. The temperatures at which characteristic changes of the shape occur are recorded. The characteristic temperatures are defined in [Clause 3](#). Vivid images in [Annex C](#) show examples of the characteristic temperatures.

For some ashes produced at 550 °C it can be difficult to determine the deformation temperature due to liberation of carbon dioxide from carbonates in the ashes, creating strong shrinkage of the test pieces. Ashing at higher temperatures removes carbonates from the ash but also removes possible contents of low melting salts. For some purposes (as e.g. searching for glass melting problems regarding wood pellets) alternative ashing temperatures of (710 ± 10) °C or (815 ± 10) °C may be used provided it is specified in the test report.

5 Reagents

5.1 Ethanol, with a purity ≥ 95 %.

5.2 Gold wire, of diameter 0,5 mm or larger, or **gold plate**, of thickness 0,5 mm to 1,0 mm with a purity of 99,99 % or a certified melting point (e.g. 1 064 °C).

5.3 Nickel wire, of diameter 0,5 mm or larger, or **nickel plate**, of thickness 0,5 mm to 1,0 mm, with a purity of 99,9 % or a certified melting point (e.g. 1 455 °C).

NOTE Nickel is used for calibration in reducing atmosphere only.

5.4 Palladium wire, of diameter 0,5 mm or larger, or **palladium plate**, of thickness 0,5 mm to 1,0 mm with a purity of 99,9 % or a certified melting point (e.g. 1 554 °C).

5.5 Carbon dioxide, carbon monoxide, hydrogen or ready mixture of carbon dioxide and carbon monoxide with 55 % (V/V) to 65 % (V/V) carbon monoxide and 35 % (V/V) to 45 % (V/V) carbon dioxide or **ready mixture of hydrogen and carbon dioxide** with 45 % (V/V) to 55 % (V/V) hydrogen and 45 % (V/V) to 55 % (V/V) carbon dioxide.

6 Apparatus

6.1 Dishes for ashing made of inert material, such as platinum or graphite and of such size that the test portion loading does not exceed 1 g/cm² of bottom area can be used for all biomass material. Before the first use, the dish shall be heated to ashing temperature for 60 min and shall cool down to ambient temperature before use. The material of the dish shall not react with the sample or ash of the sample. When using dishes of other materials (e.g. porcelain) it shall be checked that no reaction with the ashes/biomass material occurs during ashing process, i.e. the ash should be a loose powder (no sintering or melt) and the surface of the dishes shall be intact after the ashing.

6.2 Furnace for ashing, which shall be capable of providing a zone of uniform heat at the temperatures required and reaching these temperatures within the specified times. The air exchange in the furnace shall be sufficient to remove the flue gasses SO₂ and CO₂ formed during decomposition of the biofuel before these gases react with the ash components during the heating procedure.

NOTE For preparation of coal ashes according to ISO 1171, 5 to 10 air changes/min are necessary to eliminate reaction of SO₂ and CO₂ with the ash. For biomass there is currently no scientific proof for the influence of air exchange in the ashing furnace on the ash melting results although an influence is expected. Biomass usually has a lower ash content and ash is of light weight in comparison to coal ash. This property can cause the ash to be blown from the ashing crucible which can limit air exchange possibilities. A sensitivity analysis of variation of these parameters on the result of ash melting behavior can be valuable for a certain set-up.

6.3 Sample containers or bags, airtight, suitable for holding (1 to 10) g of ashed sample leaving minimum free air space e.g. LDPE zip -lip bags or max. 50 ml wide-mouth HDPE bottles.

6.4 Furnace for ash melting behaviour, electrically heated, which satisfies the following conditions:

a) it shall be capable of reaching the maximum temperature of at least 1 500 °C);

- b) it shall provide an adequate zone of uniform temperature in which to heat the test piece(s);
- c) it shall provide means of heating the test piece(s) at a uniform rate from 550 °C upwards;
- d) it shall be capable of maintaining the required test atmosphere (see [Clause 7](#)) around the test piece(s);
- e) it shall provide means of observing the change of shape of the test piece(s) during heating. The requirements for the operation/design of the furnace shall be such that a provision for observing the test in low light conditions is stipulated, be that provision one of illumination or camera sensitivity.

6.5 Pyrometer, comprised of a platinum/platinum-rhodium thermocouple.

6.6 Mould, of brass, stainless steel or other suitable material for preparing an upright cylinder of height 3 mm to 4 mm and with diameter equal to the height.

6.7 Hand press with spring pressure compression, to produce the test piece.

NOTE Manufacturers of ash fusion moulds ([6.6](#)) generally provide a hand press designed to be used with the mould. Manufacturer provided hand presses are considered suitable.

6.8 Support for the test piece, of such a material that it becomes neither distorted, nor reacts with nor absorbs the ash during the determination.

Zirconium dioxide supports are suitable or a non-absorbent interface such as platinum foil can be used between the original support and the test piece. Supports of sintered alumina or fine textured mullite have shown to influence the result especially for FT due to reaction or absorption of liquid ash and should be avoided.

6.9 Flowmeters, for measuring the components of the reducing gases (see [Clause 7](#)) and/or for measuring the flow rate of the oxidizing gas.

6.10 Mortar and pestle made of agate or zirconium oxide or other adequate grinding instruments like ball mill made of abrasion resistant material.

6.12 Optical instrument, which enables the profile of the test piece to be observed throughout the determination by using a camera or video equipment.

7 Test atmosphere

An oxidizing or reducing atmosphere during ash melting test may be used depending on the condition within the combustion system and/or as requested. An oxidizing atmosphere is obtained with air or carbon dioxide introduced into the oven at a linear rate of flow past the test piece between 100 mm/min to 250 mm/min, calculated at ambient temperature. The reducing atmosphere is obtained by introducing a mixture of

- a) 55 % (V/V) to 65 % (V/V) carbon monoxide with 35 % (V/V) to 45 % (V/V) carbon dioxide or
- b) 45 % (V/V) to 55 % (V/V) hydrogen with 45 % (V/V) to 55 % (V/V) carbon dioxide into the furnace at the same flow rate as for oxidizing atmosphere.

NOTE The flow rate is not very critical, provided that in the case of reducing atmosphere it is sufficient to prevent any leakage of air into the furnace. However, the same flow rate level is recommended also for oxidizing atmosphere. For furnaces with larger diameter a flow around 400 mm/min for reducing atmosphere can be necessary. In all cases refer also to manufacturer instructions. The flow rate for rotameter adjustment can be calculated by multiplying the flow rate in mm/min with the inside cross-section area of the furnace tube and converting to units litres/min.

WARNING — When using the reducing atmosphere given above, the gases emerging from the furnace will contain a proportion of carbon monoxide; it is essential, therefore, to ensure that these gases are vented to the outside atmosphere, preferably by means of a hood or an efficient fan system. If hydrogen is used in the reducing atmosphere, great care shall be taken to prevent an explosion, by purging with carbon dioxide both prior to the introduction of the hydrogen and after the hydrogen supply is shut off. Where a pre-prepared mix of carbon dioxide and hydrogen is used for the test atmosphere nitrogen gas can be used for the purpose of purging.

8 Calibration check

Check the pyrometer at least once a year and when required e.g. after changing heating elements under routine test conditions by observations of the melting point of gold (5.2) and, if possible in the maximum temperature of the furnace (6.4), the melting point of palladium (5.4). Place the reference wire at different locations in the oven. Test the reducing atmosphere by observing the melting point of nickel (5.3).

If the observed melting points for gold or palladium differ by more than 10 °C from the melting points of the materials given in 5.2 and 5.4 readjust or recalibrate.

An alternative to the observations of the melting points of gold and palladium is to check the pyrometer using a thermocouple certified by a recognized reference laboratory or with a calibration which is traceable back to a standard reference laboratory.

If the observed melting point for nickel differs by more than 10 °C from the melting point given in 5.3, it can be due to oxidation of nickel caused by an insufficiently reducing atmosphere. Examine the apparatus for leakages, control the flow rate and the quality of the gases and recheck the melting point of nickel.

NOTE The correct melting point of nickel is not a guarantee that the composition of the reducing atmosphere is correct, as deviations could be considerable before the fusibility is affected.

9 Procedure

9.1 Preparation of ash

Load a sufficient amount of the analysis sample of the solid biofuel in the ashing dish or dishes (6.1) to obtain a minimum of 1 g ash and spread in an even layer over the bottom surface. The use of additives to ensure complete combustion is not allowed. Continuous ashing by refilling of the sample on the previous ash in the crucible is also not allowed.

Place the dish(es) in the cold furnace (6.2) and heat in air atmosphere in accordance with the following temperature program.

- Raise the furnace temperature evenly to a temperature between 230 °C and 250 °C with a heating rate of (3 to 5) °C/min. Maintain temperature at this level for at least 180 min to allow the volatiles to leave the sample. The sample shall not ignite during this step of preparation of the ash. Do not open the furnace to check! An evidence of ignition is a sudden rise of oven temperature. If the sample ignites repeat the ashing procedure with a lower heating rate and/or a lower hold temperature.
- Continue to raise the furnace temperature evenly to (550 ± 10) °C (or to an alternative higher final ashing temperature ±10 °C) with a heating rate of ~10 °C/min. Maintain temperature at this level for at least 120 min.
- Stop heating and let cool down the furnace with sample to below 200 °C.

Remove the dish with its content from the furnace. Allow the dish and its content to cool on a heat resistant plate to ambient temperature. Either proceed with preparation of test pieces or store the sample in sample containers or bags (6.3).

If the ash started sintering during ashing at alternative temperatures, the ash shall be discarded and ashing of the sample shall be repeated applying the procedure described above with an ashing temperature of 550 °C.

If there is any doubt of incomplete ashing, ashing shall be continued at 550 °C until complete ashing is obtained.

It is recommended to prepare the ash overnight and continue with the preparation of test pieces the next morning.

9.2 Preparation of test pieces

Grind the ash in a mortar (6.10) as fine as possible. None of the ash shall be lost during grinding. Too coarse particle size will cause problems during preparation of a usable test piece. The test piece shall have a sharp outline that does not fall apart during mounting and heating.

Moisten sufficient quantity of the prepared ash with ethanol (5.1), make into a paste and press into the mould (6.6) with a spring press (6.7). Allow the test piece to dry and mount it on its support as vertically as possible (6.8).

Liquids other than ethanol can only be used if ethanol does not provide a suitable test piece. Dextrine shall not be used. Water shall not be used since chemical reactions may change the ash melting behaviour.

The test piece shall be shaped into an upright cylinder of height 3 mm to 4 mm and with diameter equal to the height. The test piece shall have sharp edges to facilitate observation.

Standards for other solid fuels allow different shaped test pieces like pyramids, truncated cones or cylinders of larger dimensions (e.g. ISO 540). These shapes are not acceptable for this test method.

9.3 Determination of characteristic temperatures

Prepare the test piece according to 9.2.

Transfer the test piece(s) on its support (6.8) to the furnace at room temperature (6.4) and adjust the composition and flow rate of the atmosphere according to Clause 7. If additional determinations are required, either they can be done in a single run or in separate runs. Test runs may be started at elevated temperatures provided they are started at least 50 °C lower than the ashing temperature.

Heat the test piece(s) with a uniform rate of 5 to 10 °C/min from ambient temperature to the final temperature.

Take a reference picture at 550 °C (or at ashing temperature if sample was not ashed at 550 °C) and then at least every 5 °C during the whole test. Record the temperatures at which the characteristic changes in shape occur (see Clause 3). Not all characteristic temperatures will be measurable for some sample types. Test pieces with very high ash melting temperatures cannot melt before the thermal capacity of the furnace is exceeded. In such cases the characteristic temperature(s) shall be recorded as greater than the thermal capacity of the furnace (e.g. FT >1 500 °C).

NOTE 1 For some herbaceous biofuel ashes strong swelling can be observed. In such cases it is strongly recommended to manually check the characteristic temperatures by an experienced analyst.

NOTE 2 With some ashes, difficulties can be encountered such as blistering, distortion, shrinkage, swelling, non-wetting of the support (caused by high surface tension) and bursting of internal gas bubbles. In such cases it is recommended to record these phenomena and possibly repeat the experiment using a different type of support.

10 Precision of the method

The achievable performance of the method is given in [Annex B](#), showing the results obtained by an international laboratory comparison study carried out for three different biomass samples (corn cob, forest residues and high-quality wood pellets). These three samples represent herbaceous and woody biomass.

11 Test report

The test report shall include at least the following information:

- a) identification of the laboratory performing the test and the date of the test;
- b) identification of product (sample) tested;
- c) a reference to this document i.e. ISO 21404:2020;
- d) ashing temperature used;
- e) the type of the atmosphere (reducing or oxidizing);
- f) the characteristic temperatures of interest (at least DT and FT), rounded to the nearest 10 °C; if a characteristic temperature of interest cannot be determined it shall be noted;
- g) any unusual observation noted during the test procedure, especially if swelling occurs during determination;
- h) any deviation from this document.

Annex A (informative)

Definition of shape factor

The shape factor (F in the formula below) of the test piece is determined when a computer is used for image analysis of the test piece during heating. In order to determine the shape factor, the circumference of a perfect semicircle (b) with the same area (A') as the test piece's shadow (A) is calculated. This ideal circumference is then put in relation to the actual measured circumference of the test piece (a). This relation gives the shape factor (see Figure A.1)

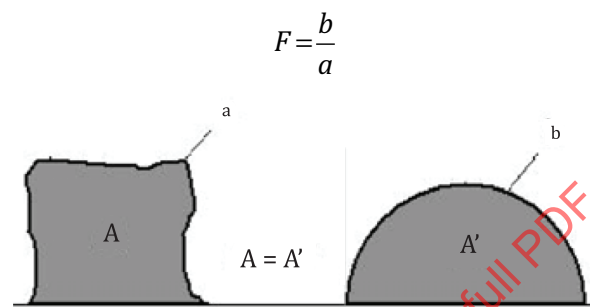


Figure A.1 — Schematic of the definition of shape factor

Annex B (informative)

Performance data

The round robin was carried out by laboratories in Austria, Belgium, Canada, Denmark, Finland, France, Germany, Italy, Lithuania, Latvia, the Netherlands, Spain, Sweden, Switzerland, the United Kingdom and the USA. The variety of instruments were used in accordance with the quality parameters specified in the method.

All participating laboratories conducted the test on three samples: corn cob, forest residues and wood pellets according to a draft of this standard based on CEN/TS 15370-1^[3]. The sample “Corn cob” was obtained from oil producing industry in Austria; sample “forest residues” was obtained from an Austrian recycling company. Both samples were prepared according to ISO 14780. They were dried and milled to <1 mm by means of cutting and cross beater mills. Ashing temperature was 550 °C. The sample “high quality wood pellets” was obtained from a wood pellet manufacturer in Ireland and was used without any particle size reduction. Ashing temperature was 815 °C. Characteristic temperatures were determined in oxidizing atmosphere.

The performance data according to ISO 5725-2 are presented in [Table B.1](#) to [Table B.4](#).

NOTE 1 See [Table B.1](#) for definition of the symbols used in [Table B.1](#) to [Table B.4](#).

NOTE 2 A guideline can be found in ISO 16993^[4], Annex C on how to use these validation parameters.

Table B.1 — Performance data for shrinkage starting temperature (SST)

Sample	n	I	o %	$\bar{X}$ characteristic temperature °C	S_R temperature °C	S_r temperature °C
corn cob	22	57	6,0	797	116	12
forest residues	19	48	8,9	1 227	43	16
wood pellets	22	51	5,7	1 170	66	11

Definition of symbols	
n	is the number of laboratories after outlier elimination
I	is the number of outlier free individual analytical values
o	is the percentage of outlier values form replicate determination
$\bar{X}$	is the overall mean
S_R	is the reproducibility standard deviation
S_r	is the repeatability standard deviation

Table B.2 — Performance data for start of deformation temperature (DT)

Sample	<i>n</i>	<i>I</i>	<i>o</i> %	<i>X</i> characteristic temperature °C	<i>S_R</i> temperature °C	<i>S_r</i> temperature °C
corn cob	21	55	6,3	1 063	96	11
forest residues	23	58	1,3	1 298	72	15
wood pellets	24	54	5,2	1 242	17	7

Table B.3 — Performance data for start of hemisphere temperature (HT)

Sample	<i>n</i>	<i>I</i>	<i>o</i> %	<i>X</i> characteristic temperature °C	<i>S_R</i> temperature °C	<i>S_r</i> temperature °C
corn cob	25	69	2,8	1 260	41	10
forest residues	23	60	4,1	1 363	71	14
wood pellets	25	64	2,2	1 276	24	11

Table B.4 — Performance data for start of flow temperature (FT)

Sample	<i>n</i>	<i>I</i>	<i>o</i> %	<i>X</i> characteristic temperature °C	<i>S_R</i> temperature °C	<i>S_r</i> temperature °C
corn cob	25	67	2,9	1 333	71	18
forest residues	27	63	3,5	1 405	87	12
wood pellets	24	60	4,1	1 296	30	11