
**Solid biofuels — Determination of
self-heating of pelletized biofuels —**

**Part 1:
Isothermal calorimetry**

*Biocombustibles solides — Détermination de l'auto-échauffement des
granulés de biocombustibles —*

Partie 1: Détermination calorimétrique isotherme

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

A list of all parts in the ISO 20049 series can be found on the ISO website.

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

There is a continuous global growth in production, storage, handling, bulk transport and use of solid biofuels especially in the form of pelletized biofuels.

The specific physical and chemical characteristics of solid biofuels, their handling and storage can lead to a risk of fire and/or explosion, as well as health risks such as intoxication due to exposure to carbon-monoxide, asphyxiation due to oxygen depletion or allergic reactions.

Heat can be generated in solid biofuel by exothermic biological, chemical and physical processes. Biological processes include the metabolism of fungus and bacteria and occur at lower temperatures; the oxidation of wood constituents increases with temperature and dominates at higher temperatures; the heat production from biological and chemical processes leads to transport of moisture in the bulk material, with associated sorption and condensation of water, which both are exothermic processes. In, for example, a heap of stored forest fuel or a heap of moist wood chips, all of these processes can be present and contribute to heat production.

Solid biofuels such as wood pellets, however, are intrinsically sterile^[1] due to the conditions during manufacturing (exposure to severe heat during drying, fragmentation during hammermilling and pressure during extrusion) but can attract microbes if becoming wet during handling and storage resulting in metabolism and generation of heat. Leakage of water into a storage of wood pellets can also lead to the physical processes mentioned above. Non-compressed wood like feedstock and chips typically have a fauna of microbes which under certain circumstances will result in heating. All the processes mentioned above contribute to what is called self-heating although oxidation is likely to be one of the main contributing factors in the temperature range under which most biofuels are stored. The heat build-up can be significant in large bulk stores as the heat conduction in the material is low. Under certain conditions the heat generation can lead to thermal runaway and spontaneous ignition.

The potential for self-heating seems to vary considerably for different types of solid biofuel pellets. The raw material used, and the properties of these raw materials have proven to influence the propensity for self-heating of the produced wood pellets. However, the production process (e.g. the drying process) also influences the potential for self-heating. It is therefore important to be able to identify solid biofuel pellets with high heat generation potential to avoid fires in stored materials.

Two intrinsically different types of tests methods can be used to estimate the potential of self-heating;

- a) In the isothermal calorimetry method described in this document, the heat flow generated from the test portion is measured directly.
- b) In basket heating tests, the temperature of the test portion is being monitored and the critical ambient temperature (CAT), where the temperature of the test portion just does not increase significantly due to self-heating, is used for indirect assessment of self-heating.

These two methods are applied at different analysis temperature regimes. The operating temperature for an isothermal calorimeter is normally in the range 5 °C to 90 °C whereas basket heating tests are conducted at higher analysis (oven) temperatures. For basket heating tests with wood pellets, CATs are found for a 1 l sample portion in the range 150 °C to 200 °C.

The application of the test data should thus be identified before selecting the appropriate analytical method.

NOTE 1 The two types of test methods referred to above do not measure heat production from physical processes such as transport of moisture.

NOTE 2 It is likely that oxidation reactions taking place in the low respective high temperature regimes for solid biofuel pellets are of different character and thus have different reaction rates and heat production rates. In such a case, extrapolation of the data from a high temperature test series can lead to non-conservative results and might not be applicable without taking the low temperature reactions into account. In the general case of two reactions with different activation energies, the high activation energy is “frozen out” at low temperatures and the low activation energy reaction is “swamped” at higher temperatures^[2].

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NOTE 3 It has been shown for a limited number of different types of wood pellets that the reaction rates in the lower temperature regime measured by isothermal calorimetry were higher compared to the reaction rate data determined from basket heating tests in the higher temperature regime^[3].

Isothermal calorimetry is used for determination of the thermal activity or heat flow of chemical, physical and biological processes. The method described in this document is developed for the measurement of heat flow from the self-heating of solid biofuel pellets, but the technique is most commonly used in the fields of pharmaceuticals, energetic materials, and cement^[3] to ^[Z].

Data from the isothermal calorimetry screening test procedure included in this document is intended for comparison of the spontaneous heat generation (self-heating) of solid biofuel pellets ([Annex B](#)).

Guidance is additionally given on the use of isothermal calorimetry test data for the calculation of the overall reaction rate of the heat producing reactions ([Annex C](#)).

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Solid biofuels — Determination of self-heating of pelletized biofuels —

Part 1: Isothermal calorimetry

1 Scope

This document:

- a) specifies a general test procedure for quantification of the spontaneous heat generation from solid biofuel pellets using isothermal calorimetry;
- b) specifies a screening test procedure for wood pellets using an instrument temperature of 60 °C;
- c) establishes procedures for sampling and sample handling of solid biofuel pellets prior to the analysis of spontaneous heat generation; and
- d) gives guidance on the applicability and use of isothermal calorimetry for calculation of the net reaction rate of the heat producing reactions of solid biofuel pellets.

The test procedure given in this document quantifies the thermal power (heat flow) of the sample during the test, it does not identify the source of self-heating in the test portion analysed.

Data on spontaneous heat generation determined using this document is only associated with the specific quality and age of the sample material. The results are product specific.

This document is applicable to solid biofuel pellets only.

The information derived using this document is for use in quality control and in hazard and risk assessments related to the procedures given in ISO 20024:2020.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 14780, *Solid biofuels — Sample preparation*

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

ISO 18135, *Solid Biofuels — Sampling*

ISO 18846, *Solid biofuels — Determination of fines content in quantities of pellets*

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 <https://www.iso.org/obp>

— IEC Electropedia: available at <http://www.electropedia.org/>

**3.1
analysis temperature**

temperature of the analysis environment, i.e. the calorimeter temperature

**3.2
self-heating**

rise in temperature in a material resulting from an exothermic reaction within the material

[SOURCE: ISO 13943:2017, 3.341, modified — “<chemical>” omitted at the beginning of the definition.]

**3.3
spontaneous ignition**

ignition caused by an internal exothermic reaction

[SOURCE: ISO 13943:2017, 3.24]

Note 1 to entry: See definitions of ignition in ISO 13943.

**3.4
test portion**

sub-sample either of a *laboratory sample* (3.6) or a *test sample* (3.5)

[SOURCE: ISO 16559:2014, 4.202]

**3.5
test sample**

laboratory sample (3.6) after an appropriate preparation made by the laboratory

[SOURCE: ISO 16559:2014, 4.203]

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**3.6
laboratory sample**

combined sample or a sub-sample of a combined sample for use in a laboratory

[SOURCE: ISO 16559:2014, 4.124]

**3.7
thermal power**

heat rate produced by the sample during the test and commonly expressed, with reference to the unit mass of pelletized biofuel, in W/g or J/(s · g)

[SOURCE: CEN/TR 16632:2014, 8.3, modified — substitution of "cement" with " pelletized biofuel".]

4 Principle

Isothermal calorimetry is a sensitive technique for studying heat production or heat consumption from samples of different kinds. It is non-destructive and non-invasive to the sample. When heat is produced in a sample, an isothermal heat conduction calorimeter (here isothermal calorimeter) measures the thermal power (heat flow). The sample is placed in an ampoule that is in contact with a heat flow sensor that is also in contact with a heat sink. When heat is produced or consumed by any process, a temperature gradient is developed across the sensor. This will generate a voltage, which is measured. The voltage is proportional to the heat flow across the sensor and to the rate of the process taking place in the sample ampoule. This signal is recorded continuously and in real time.

NOTE 1 A commercial instrument for isothermal calorimetry normally has multiple channels and can thus be used for measurements of several samples simultaneously.

For each sample (channel) there is an inert reference that is on a parallel heat flow sensor. During the time that the heat flow is monitored, any temperature fluctuations entering the instrument will

influence both the sample and the reference sensors equally. This architecture allows a very accurate determination of heat that is produced or consumed by the sample alone while other non-sample related heat disturbances are efficiently removed. The measured heat flow is normalized against the weight of the sample and the result is expressed in mW/g.

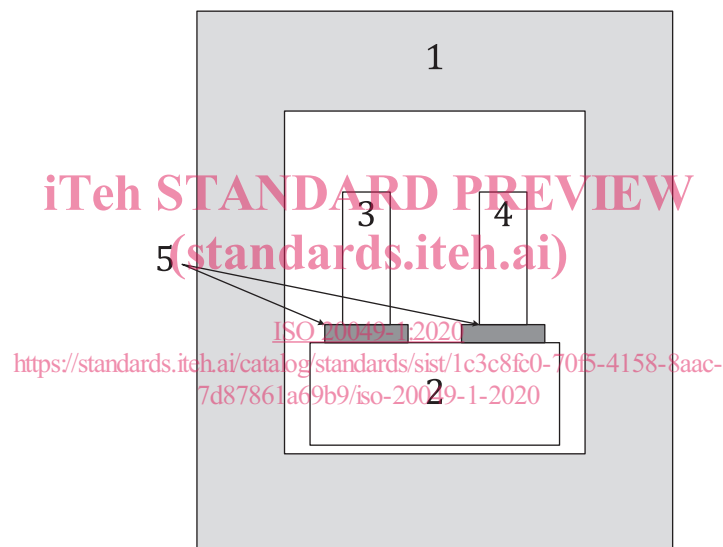
NOTE 2 The operating temperature for an isothermal calorimeter is normally in the range 5 °C to 90 °C. However, there are calorimeters with somewhat higher span for operating temperature.

NOTE 3 The moisture content of the bio pellet sample could have an impact on the test result. The extent of this impact is not known at the time of publication of this document.

5 Apparatus

The usual laboratory apparatus and, in particular, the following.

5.1 Isothermal calorimeter, consisting of a sample holder for the sample vial and the reference vial, each thermally connected to heat flow sensors, which are thermally connected to a constant temperature sink. See example in [Figure 1](#).



Key

1	thermostat	4	reference
2	heat sink	5	heat flow sensors
3	sample		

Figure 1 — Schematic drawing of an isothermal calorimeter

The calorimeter shall be calibrated at the analysis temperature (see [Annex A](#)). The analysis temperature for the screening test procedure shall be 60 °C.

The baseline shall exhibit a low random noise level and be stable against drift (see [Annex A](#)).

The minimum sensitivity for measuring power output shall be 100 µW.

The data acquisition equipment shall be capable of performing continuous logging of the calorimeter output measured at minimum time interval of 10 s.

5.2 Vials, made of glass with a minimum volume of 20 ml and provided with an air tight lid with an inert seal.

Vials with volumes other than 20 ml can be used if the sample loading is scaled accordingly (see 7.2.1). In such cases this deviation from the standard procedure shall be noted in the test report.

5.3 Balance, with a resolution of at least 10 mg.

6 Sample handling

6.1 General

Correct sample handling is important in maintaining the properties of solid biofuel pellets samples. The transport and storage (see 6.3) are of special importance for self-heating properties as the reactivity of the sample will be reduced from prolonged exposure to air oxygen. This is further accentuated at exposure to elevated temperatures.

The sample history and the conditions for sample handling should be stated as thoroughly as possible in the test report.

6.2 Sampling

Sampling of solid biofuel pellets shall be made according to procedures prescribed in ISO 18135.

The minimum size of the laboratory sample is 500 ml.

6.3 Sample transport and storage

The laboratory sample shall be transported in a closed airtight sample container.

NOTE 1 An airtight container is used to limit the amount of available oxygen in order to reduce oxidation reactions with the sample.

The container shall be completely filled with sample.

NOTE 2 A completely filled container limits the amount of air in the container (i.e. the amount of oxygen) and further reduces deteriorations of the sample from physical wear (i.e. reduces the amount of fine fraction).

The time between sampling and analysis shall be minimized and elevated temperatures shall be avoided.

NOTE 3 It has been seen that a sample can be stored for several months without any significant changes in reactivity if put in a freezer directly after received at the analysis lab.

6.4 Sample preparation

Any fine fraction shall be removed from the laboratory sample to create a test sample before extracting test portions. The fine fraction can be removed by gentle hand sieving using sieve size 3,15 mm in accordance with ISO 18846.

NOTE Fine fraction are removed to avoid that fine fraction produced during the handling and transport is included in the test portion.

The test portion shall be randomly taken from the test sample. Procedures from ISO 14780 shall be followed.

7 Test procedure

7.1 Temperature stabilisation

Set the instrument temperature to the selected analysis temperature. The analysis temperature for the screening test procedure is 60 °C.

Follow the manufacturers procedure to ascertain the temperature stability.

NOTE The values for stability criterion vary for different calorimeters and are usually decided by the software.

7.2 Sample vial preparation

7.2.1 Preparation procedure

The prepared sample vial shall not be pre-heated.

NOTE 1 Pre-heating of the sample vial is often used to reduce the disturbance in the measurement signal from thermal imbalance between the sample and the calorimeter. However, pre-heating is not applied in this test procedure as it was seen during a preliminary interlaboratory study (ILS) that pre-heating was not favourable for measurement uncertainty in this application.

Handle the sample using a pair of tweezers or rubber gloves to avoid contamination of the sample.

Use whole pellets or larger pieces of pellets if possible.

Weigh into the sample vial (5.2) a test portion of 0,2 g pellets per ml volume of the glass vial used. For example, use $4 \pm 0,1$ g pellets for a 20 ml glass vial.

NOTE 2 It has been shown for wood pellets that there is no significant difference in measured thermal power for measurements made on whole pellets versus smaller parts of pellets (mixture from 2 mm particles and less)^[8].

Tighten the lid of the sample vial properly after sample loading.

If oxygen deficiency which influences the test results is occurring in the closed ampoule during measurement, follow the procedure in 7.2.2. A method to detect significant oxygen deficiency is given in 8.1.

NOTE 3 It has been shown that oxygen deficiency in the closed vial normally does not influence the measured heat production significantly in measurements with wood pellets using the screening test procedure prescribed in this document^[8]. However, in certain cases with highly reactive pellets oxygen deficiency can influence the test results.

7.2.2 Procedure to find proper test portion mass in case of influence from oxygen deficiency

To find the proper sample mass for avoiding the influence of oxygen deficiency, first run tests with 4 g and 2 g sample mass (in case of using a 20 ml sample vial). If the difference in normalized total heat production between the two sample weights (4 g and 2 g) is non-significant (less than 10 relative-% difference) no more tests are required; 4 g sample mass is proper to use. If, however, the difference is significant additional tests with 1 g and 3 g sample weight shall be made to find the sample mass where the effect of oxygen deficiency is non-significant.

7.3 Reference vial preparation

Prepare two reference vials for each sample vial (for each channel).

The portion of reference material shall have the same total heat capacity as the test portion. Water is recommended as reference material although other non-reactive materials could be used, for example dry quartz sand.

A standard 20 ml glass vial filled with 1,3 g of deionized water can be used as reference vial for testing 4,0 g of wood pellet.

NOTE The heat capacity of wood pellets ($\approx 6,5$ wt-% moisture content) has been reported to be in the range of $1,2 \text{ J}/(\text{g}\cdot\text{K})$ ^[2] to $1,6 \text{ J}/(\text{g}\cdot\text{K})$ ^[10]. If data on the specific wood pellet sample is not available, a value of $1,4 \text{ J}/(\text{g}\cdot\text{K})$ can be assumed, which results in a reference sample of 1,3 g deionized water, appropriate for tests with 4,0 g wood pellets.

If the calorimeter is equipped with a fixed reference, the reference shall be assured to be appropriate for testing pelletized biofuels.

7.4 Measurement

7.4.1 First baseline measurement

Start the test with a baseline measurement:

- 1) Put a reference vial in the reference position. This reference shall be kept stationary for the complete test.
- 2) Put a second reference vial in the measurement position for the baseline measurement.
- 3) When the instrument has reached stable conditions, run a 30 min baseline measurement.

NOTE This applies for all channels that are used for measurement.

The baseline measurement data shall be included in the measurement data file.

7.4.2 Sample measurement

When the first baseline measurement is completed, replace the reference vial in the measurement position with the sample vial.

Measure the heat flow from the sample vial and save to the measurement data file. The measurement shall be run until the time when the heat development is no longer significantly influenced but at least for 24 h.

NOTE The procedure for starting the test and saving data to the measurement data file can differ between different brands of isothermal conduction calorimeters.

7.4.3 Second baseline measurement

After completion of the measurement on the sample:

- 1) Remove the sample vial from the measurement position.
- 2) Put a second reference vial in the measurement position.
- 3) When the instrument has reached stable conditions, run a 30 min baseline measurement.

NOTE The baseline measured after the test is to ensure that the instrument have the same stability as before the test started. There is software for some instruments that by default measure the baseline before and after the test.

7.4.4 Measurement data file

The resulting data file shall include the data from the sample measurement as well as the data from both the baseline measurements. The file shall be stored with a unique name identifying the test portion measured.