INTERNATIONAL STANDARD

ISO 20049-1

First edition
2020-05

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

Reference number
ISO 20049-1:2020(E)

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Published in Switzerland

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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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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].

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 [7].

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).

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]

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.

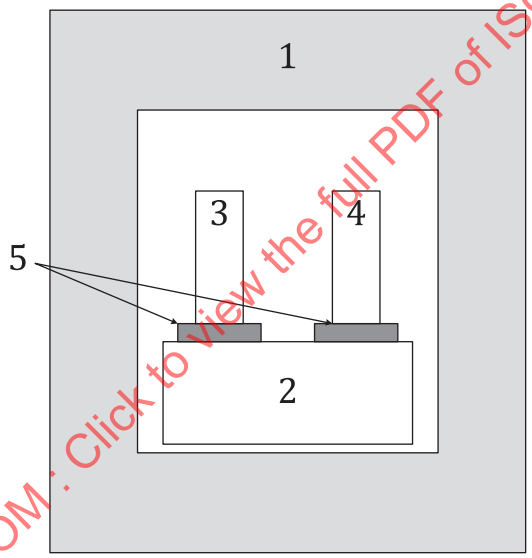
NOTE 2 The operating temperature for an isothermal calorimeter is normally in the range 5 °C to 90 °C. However, there are calorimeters with somewhat higher span for operating temperature.

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
2 heat sink
3 sample
4 reference
5 heat flow sensors

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 continues 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 ± 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 (≈6,5 wt-% moisture content) has been reported to be in the range of 1,2 J/(g·K)[9] to 1,6 J/(g·K).[10] If data on the specific wood pellet sample is not available, a value of 1,4 J/(g·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.

8 Results

8.1 Test data

The data recorded is the thermal power (heat flow) in mW. The test data shall be presented as a plot of specific thermal power in mW/g versus time.

Investigate the thermal power data plot for signs of oxygen deficiency in the ampoule during the test (see Note 1 and Note 2). If such signs are present additional tests shall be made in accordance with 7.2.2.

NOTE 1 A typical sign of significant oxygen deficiency in a test is a sharp break in the heat flow curve (see Figure D.3).

NOTE 2 The total heat production has typically reached a value of about 60 J (in a 20 ml sample vial) at the time when oxygen depletion starts to have effect on the heat production rate.

8.2 Reported data

Report the maximum peak in specific thermal power (mW/g) and the specific total heat produced (J/g) during the test.

The specific total heat is calculated by integrating the specific thermal power curve from the time of the maximum peak until (normally) 24 hours.

If significant heat production was measured for longer time than 24 h, the integration shall include also that period, and the time used for integration shall be reported.

The maximum peak is usually found in the beginning of the measurement. In cases where the thermal power increases over time and ultimately exceeds the initial peak, this later maximum value shall not be reported as the maximum peak value.

NOTE Annex B gives information on measured data from different types of solid biofuel pellets measured by isothermal calorimetry.

9 Test report

The test report shall include the following information:

a) Test laboratory:
   1) name and address of the laboratory;
   2) isothermal calorimetry instrument used.

b) Sample description:
   1) Sample ID;
   2) type of product (and brand name if appropriate);
   3) classification (if available) e.g. according to ISO 17225-2;
   4) product data (if available: diameter, length, density, moisture content, material composition);
   5) sample selection process (e.g. random);
   6) product history (date of: production, sampling, transport, and arrival to the test laboratory);

7) type of package for the sample during transport.

c) Sample preparation:

1) Sample storage prior to sample preparation (e.g. temperature);

2) date and time of unpacking and sample preparation (hour, day, month and year);

3) type of sample preparation before taking out test portions.

d) Reference to this document (ISO 20049-1):

1) Analysis temperature of the isothermal calorimeter;

2) use of the test results: screening tests or tests for calculation of kinetic parameters.

e) Any unusual features noted during the determination which may affect the result.

f) Test results of the test; including units and the basis for which they are given.

10 Repeatability and reproducibility

An interlaboratory study (ILS) was held during the years 2017-2019 with nine participating laboratories. The testing was made with three different types of wood pellets, all sampled at producers in Sweden. Valid results on measurement uncertainty were only obtained for one of the three pellet types tested. The results for the valid tests with pellet type P1 are given in Table 1 and Table 2.

More details on the ILS can be found in Annex D.

Table 1 — Measurement uncertainty for specific thermal power, q_{max}

Measured quantity	Pellet type and test portion mass	Quantity mean – m (mW/g)	Repeatability			Reproducibility		
			s_r (mW/g)	s_r/m (%)	r (mW/g)	s_R (mW/g)	s_R/m (%)	R (mW/g)
q_{max}	P1, 4 g	1,11	0,026	2,3	0,07	0,15	13,5	0,38
	P1, 3 g	1,09	0,058	5,3	0,15	0,16	14,8	0,41
	P1, 2 g	1,11	0,046	4,1	0,12	0,15	14,0	0,39
	P1, 1 g	1,09	0,052	4,8	0,13	0,14	12,8	0,35

Table 2 — Measurement uncertainty for specific total energy, q_{tot}

Measured quantity	Pellet type and test portion mass	Quantity mean – m (J/g)	Repeatability			Reproducibility		
			s_r (J/g)	s_r/m (%)	r (J/g)	s_R (J/g)	s_R/m (%)	R (J/g)
q_{tot}	P1, 4 g	17,0	0,31	1,8	0,80	0,89	5,2	2,3
	P1, 3 g	17,3	1,28	7,4	3,3	1,4	8,2	3,6
	P1, 2 g	18,0	0,49	2,7	1,2	1,0	5,4	2,5
	P1, 1 g	17,8	0,86	4,8	2,2	1,6	9,2	4,1

Annex A
(normative)

Calibration of the calorimeter

A.1 General

Calibrate the instrument according to the manufacturer's recommendations at regular intervals of one year or less, or whenever there are questions about performance.

A.2 Calibration/validation of temperature

Calibrate the instrument for the selected analysis temperature.

NOTE 1 The measurement procedure in this document can be applied for different analysis temperatures, e.g. for extended measurements at several temperatures for deriving a kinetic model of heat production (see Annex C).

Validate the set temperature by an independent measurement of the temperature in the thermostat media. The temperature shall not deviate more than 0,2 K from the set temperature.

NOTE 2 The temperature calibration is made using a calibrated thermocouple device.

A.3 Calibration of thermal power

Calibrate the thermal power measurement of the instrument at the analysis temperature.

The calorimeter shall be at equilibrium with no significant signal drift prior to the initiation of the calibration process.

NOTE 1 The measurement procedure in this document can be applied for different analysis temperatures, e.g. for extended measurements at several temperatures for deriving a kinetic model of heat production (see Annex C).

NOTE 2 The purpose of calibration is to compare the calorimeter signal with the thermal power or enthalpy change of a well-defined process, i.e. a calibration process, after which the calorimeter signal is adjusted in order to be accurate within defined and tolerable limits. The result from the calibration measurement is compared with the theoretical value that has been assigned to the calibration process and a calibration constant is calculated.

Heat flow calorimeters can be sensitive to systematic errors due to the fact that a fraction of the generated heat escapes the heat flow sensors, the magnitude of which depends on the design of the instrument. It is thus important that the calibration process is designed in a way that it closely mimics the real sample measurement. Calibration can be made electrically by generating a known amount of Joule heat in a well-positioned resistor or chemically by a reaction of well-established thermal power or enthalpy change.

Many commercial heat flow calorimeters are equipped with an inbuilt electrical heater (calibration heater) that is used to calibrate the instrument. The placement of the calibration heater in relation to the positioning of the sample and heat flow sensor can be critical for the calorimetric accuracy. The instrument manufacturer normally specifies the accuracy of the calorimeter when calibrated according to the manufacturer's instructions.

Due to minor temperature dependency of the sensitivity of the heat flow sensors within a narrow temperature range it is recommended to calibrate the calorimeter at the same set temperature as the

sample measurement is to be conducted. It is recommended to validate the accuracy achieved by the calibration by use of a well characterised independent test process[11].

A.4 Noise level and drift requirements

Requirements on noise and drift shall be verified for a new instrument and whenever there are questions about performance.

The rate of change of the baseline measured during a time period of 3 days shall be ≤20 µJ/s per gram sample per hour of the test and a baseline random noise level of ≤10 µJ/s per gram sample.

NOTE 1 In practice the baseline is measured for 3 days and a straight line is fitted to the power (J/(g·s)) versus time (h) data using a linear regression procedure. The long-term drift is then the slope in the line (J/(g·s·h)) and the baseline noise level is the standard deviation (J/(g·s)) around this regression line.

NOTE 2 The rationale for these limits is found in [12].

Annex B
(informative)

Examples of screening data

The isothermal calorimetry data presented below, see Table B.1, have been conducted in essence according to screening test procedure given in this document. A deviation was that pre-heating at 60 °C was made for 10 min.

The tests have been performed with an isothermal calorimeter at an analysis temperature of 60 °C for 24 h. With a few exceptions, the test portion has been 4 g and duplicate tests have been performed for each sample. The data presents the average from the duplicate tests.

NOTE Detailed information on the test equipment can be found in [13].

Table B.1 — Examples of peak thermal power and total heat for different sample tested at (60 °C) with isothermal calorimetry[13]. Here ranking by peak thermal power

Ranking No.	Pellet origin	Pellet type (for details on composition see[13])	Peak thermal power[a] (mW/g)	Total heat[b] (J/g)
1	Sweden	Wood pellet	1,06	18,71
2	Sweden	Wood pellet	0,91	15,04
3	Sweden	Wood pellet	0,77	13,51
4	Sweden	Wood pellet	0,69	17,53
5	Germany	Wood pellet	0,61	15,56
6	Denmark	Wood pellet	0,46	13,91
7	Sweden	Wood pellet	0,42	12,13
8	Sweden	Wood pellet	0,38	10,51
9	Sweden	Wood pellet	0,37	8,88
10	Sweden	Wood pellet	0,35	9,19
11	Germany	Wood pellet	0,31	8,16
12	Germany	Wood pellet	0,29	10,15
13	Sweden	Wood pellet	0,23	12,35
14	Sweden	Wood pellet	0,18	6,73
15	Germany	Wood pellet	0,16	6,10
16	Denmark	Wood pellet	0,16	5,58
17	Denmark	Wood pellet	0,16	5,72
18	Germany	Wine prod. residue	0,16	6,87
19	Sweden	Wood pellet	0,15	5,21
20	Austria	Wood pellet	0,14	4,89
21	Denmark	Straw/seed residue/spruce	0,14	4,26
22	Germany	Wood pellet	0,14	5,34
23	Germany	Wood pellet	0,11	3,58
24	Denmark	Wood pellet	0,11	3,81

[a] Maximum specific thermal power during the test.

[b] Specific total heat produced during the 24-h test.

NOTE "Wood pellet" is typically a mixture of pine and spruce.

Table B.1 *(continued)*

Ranking No.	Pellet origin	Pellet type (for details on composition see[13])	Peak thermal power[a] (mW/g)	Total heat[b] (J/g)
25	Sweden	Wood pellet	0,10	3,44
26	Sweden	Wood pellet	0,09	4,04
27	Denmark	Straw/seed residue/spruce	0,09	3,77
28	Germany	Wood pellet	0,09	3,66
29	Sweden	Wood pellet	0,06	2,18
30	Spain	Eucalyptus pellet	0,05	2,59
31	Germany	Eucalyptus pellet	0,05	1,70

[a] Maximum specific thermal power during the test.

[b] Specific total heat produced during the 24-h test.

NOTE "Wood pellet" is typically a mixture of pine and spruce.

Annex C
(informative)

Determination of reaction kinetics

C.1 Theory

The temperature dependence of a reaction rate coefficient (k) can be studied assuming it follows the Arrhenius equation (Formula (C.1)) and the kinetic parameters can be calculated using isothermal calorimetry data.

$$k = Ae^{\frac{-E}{RT}} \tag{C.1}$$

If the process shows a constant rate of reaction at each temperature in the isothermal calorimeter, the activation energy can be calculated from plot of ln $\dot{q}$ (thermal power) as a function of $1/T$ (T in Kelvin), *c.f.* (Formula (C.2)). Formula (C.2) is a linear equation of ln($\dot{q}$) in 1/T.

$$\ln(\dot{q}) = \ln(QA) - \frac{E}{RT} \tag{C.2}$$

where

R is the universal gas constant 8,314 J/(mol · K);

Q is the heat of reaction, J/kg;

A is the frequency factor, s^{-1}.

If the thermal power is changing during the measurement, *i.e.*, the reaction rate is influenced by the extent of the reaction during the experiment, the activation energy should be calculated using thermal powers measured at the same extent of reaction at the different temperatures investigated. The extent of reaction is proportional to the heat of the reaction, so the Arrhenius plot can be made with thermal powers assessed at the same amount of specific total heat. To obtain the kinetic parameters, thermal power needs to be measured for at least three different temperatures. A curve for ln $\dot{q}$ versus 1 000/T, can be obtained by a linear fit of the data. Activation energy, E (kJ/mol), is obtained from the slope of the linear fit, which is equal to $-E/R$. The combined term $Q \times A$ (J/(kg·s)) is obtained by taking the exponential of the intercept on the Y-axis at $1/T = 0$ (see Formula (C.2)).

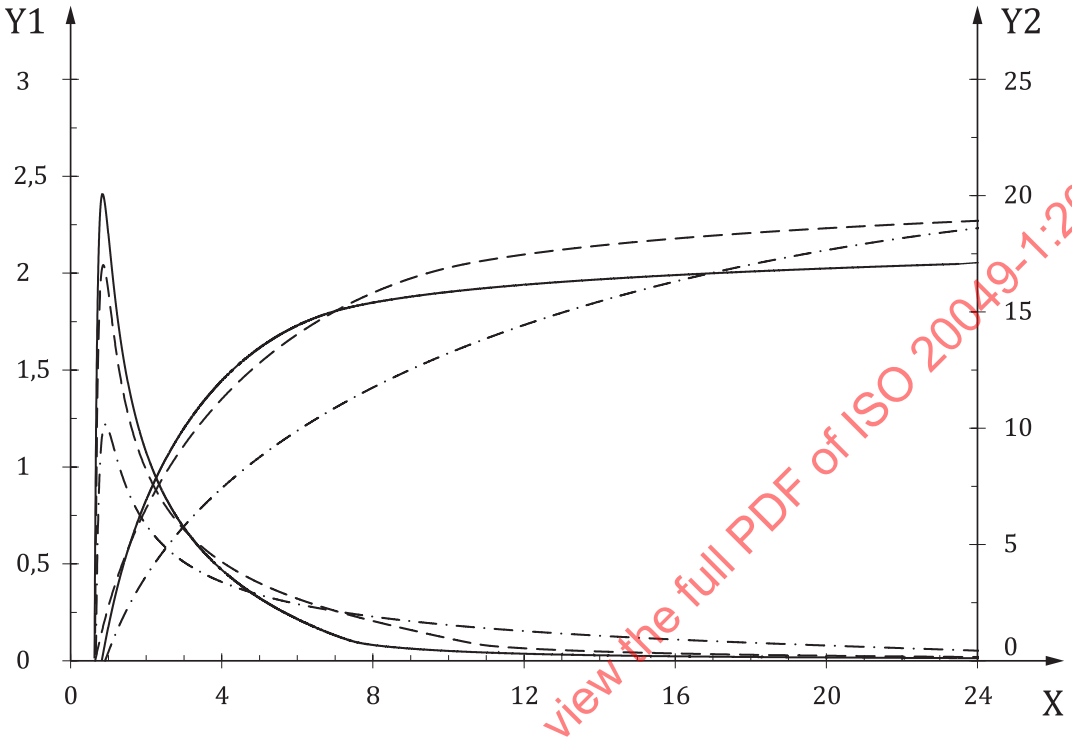
NOTE Different parts of the thermal power curves could be used for the calculation of kinetic parameters, which is shown in the following sections.

C.2 Example

This example shows how kinetic parameters have been calculated for pellet P1 (see Annex D for information on this pellet). First, the thermal power was measured using isothermal calorimetry at three different temperatures, in this case 60 °C, 50 °C and 40 °C, as shown in Figure C.1 for tests with 4 g sample mass and in Figure C.2 for tests with 2 g sample mass.

In the tests with 4 g of sample mass made at 60 °C it can be seen (*c.f.* Figure C.1) that oxygen depletion has a significant impact on the test already after 7 hours. There is a break in the heat flow curve at that time and the total heat produced is more than 60 J (4 g × ~17 J/g). This information reveals that a smaller sample portion mass would be more appropriate in this case for the task of calculating kinetic parameters for the temperature range studied.

The data from tests with 2 g of sample mass will be used here in the following. The heat flow curves at the different temperatures together with the specific total heat during these tests are shown in Figure C.2. It can be seen from this figure, that for this sample mass the total produced heat after 24 hours is just below 60 J even in the 60 °C test (2 g × ~29 J/g). There are thus no signs of significant effect from oxygen depletion for this sample mass and the signal from the measurements is high enough for all temperatures.

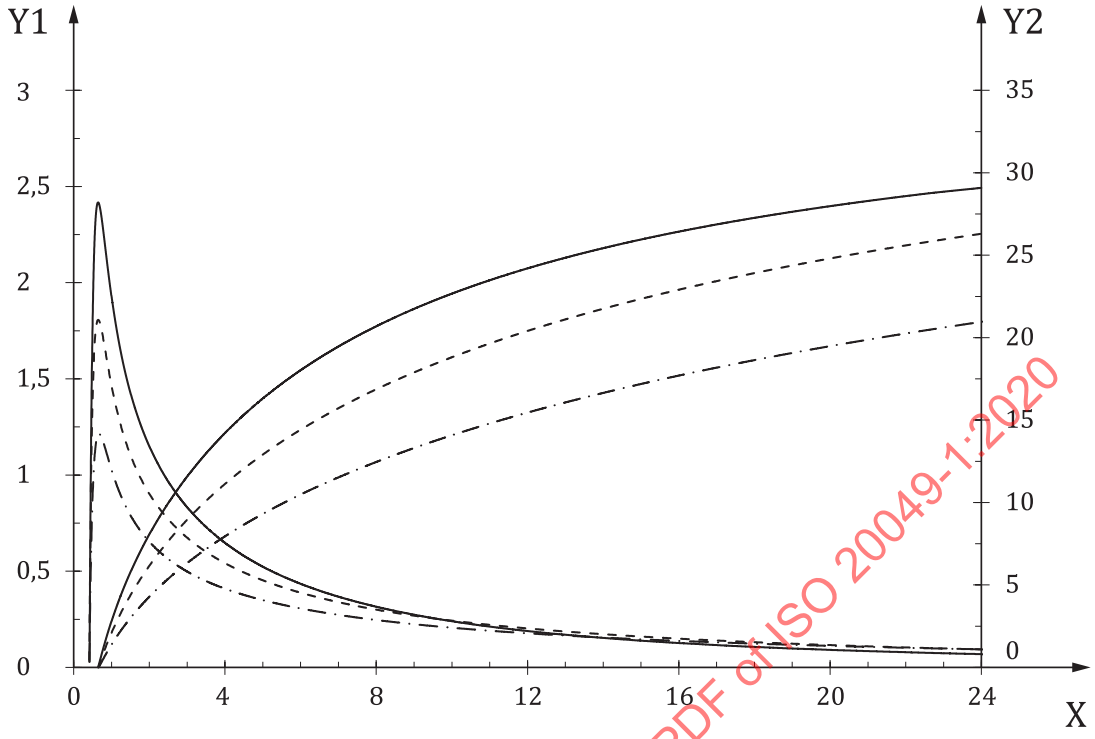


Key

Y1	specific thermal power (heat flow) (mW/g)
Y2	specific total heat (J/g)
X	time (hour)
———	P1_4g_60 °C
— —	P1_4g_50 °C
— · —	P1_4g_40 °C

NOTE The integration of specific total heat is started from the initial peak of the specific thermal power.

Figure C.1 — Test with pellet P1 with 4 g sample mass at 60 °C, 50 °C and 40 °C



Key

Y1	specific thermal power (heat flow) (mW/g)
Y2	specific total heat (J/g)
X	time (hour)
———	P1_2g_60 °C
– – – –	P1_2g_50 °C
— · —	P1_2g_40 °C

NOTE The integration of specific total heat is started from the initial peak of the specific thermal power.

Figure C.2 — Test with pellet P1 with 2 g sample mass at 60 °C, 50 °C and 40 °C

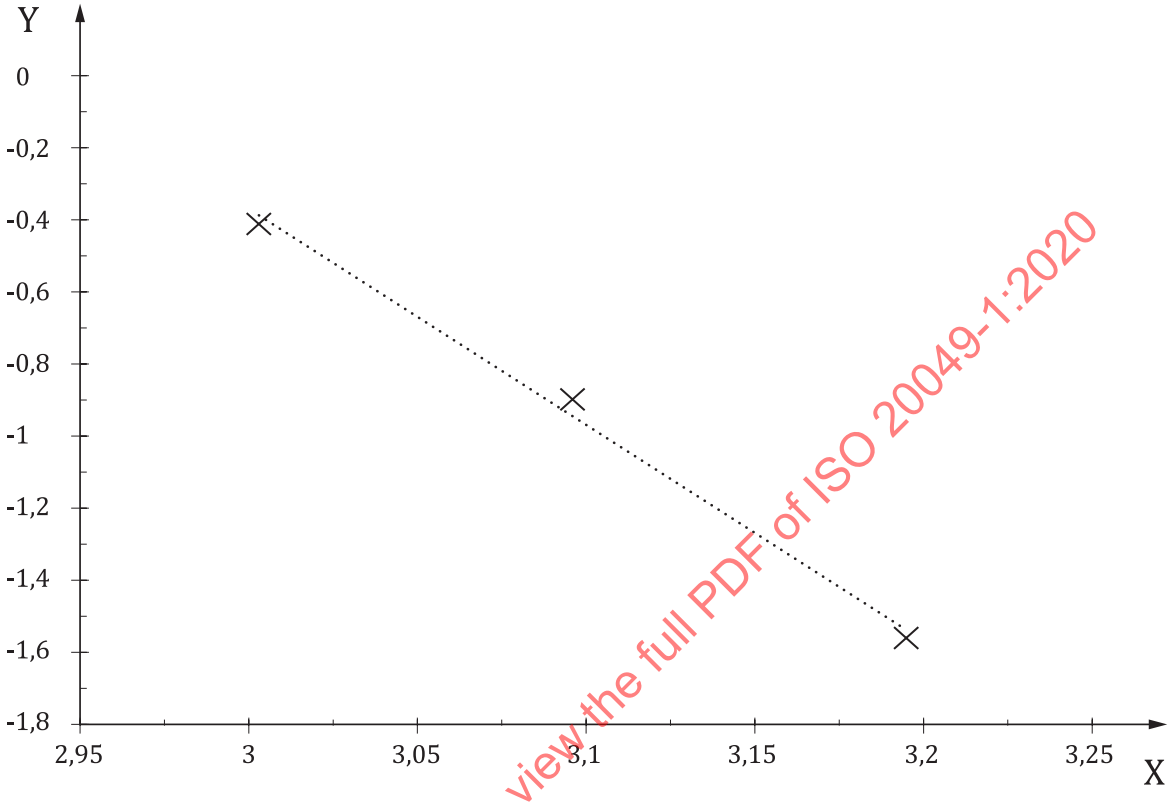
The next step is to select a series of data (triplet) of thermal powers for the same extent of reaction from the different temperature runs. Theoretically, it would be enough to select one single data triplet, if the influence of interferences was known. Such data would be found from the measurements at a time after that disturbance from thermal imbalance has ceased and before influence from oxygen depletion starts to be significant. However, to make certain that the correct data is used for describing the reaction rate, it is best to calculate the reaction parameters based on data from multiple points for the different extent of the reaction. This is made as an example in Table C.1 for P1, based on the data from the tests with 2 g of sample mass.

The specific thermal power measured at the three different temperatures are tabulated in Table C.1 for a wide range of values of equivalent extent of reaction, i.e., from the same value of specific total heat (J/g) at the different temperatures. The lowest value of specific total heat in Table C.1 is selected to occur after the maximum of the initial peak in the measurements at each temperature.

Table C.1 — Specific thermal power ($\dot{q}_{max}$) at 40 °C, 50 °C and 60 °C for 2 g sample mass for pellet P1 at different values of specific total heat (J/g)

Specific total heat (J/g)	Specific $\dot{q}$ (mW/g)		
	60 °C	50 °C	40 °C
0,2	2,41	1,79	1,21
0,4	2,39	1,78	1,19
0,6	2,37	1,75	1,16
0,8	2,35	1,72	1,13
1	2,31	1,68	1,09
2	2,10	1,48	0,93
4	1,70	1,15	0,68
6	1,39	0,92	0,52
8	1,16	0,74	0,41
10	0,96	0,61	0,32
12	0,80	0,50	0,26
14	0,66	0,41	0,21
16	0,54	0,33	0,17
18	0,44	0,27	0,13
20	0,34	0,21	0,11

From the data in Table C.1, $\ln(\dot{q})$ is plotted versus 1 000/T for the three different temperatures, see Figure C.3 for an example of such a plot of data from a specific total heat of 14 J/g.



Key

Y $\ln(\dot{q})$ (mW/g)

X 1 000/T (1/K)

$y = -6{,}033\ 1x + 17{,}728$

Figure C.3 — Example of plot of ln $\dot{q}$ versus (1000/T) for pellet P1

From the data in Figure C.3 and (Formula (C.2)), it is possible to calculate the activation energy (E) and $Q \times A$. The activation energy E is obtained from the slope of the line, which is equal to $-E/R$ and the intercept of the Y-axis represents $\ln(Q \times A)$. These calculations were made from the data in Table C.1, and the results from the plots (one plot for each extent of reaction) together with the resulting reaction parameters are presented in Table C.2.

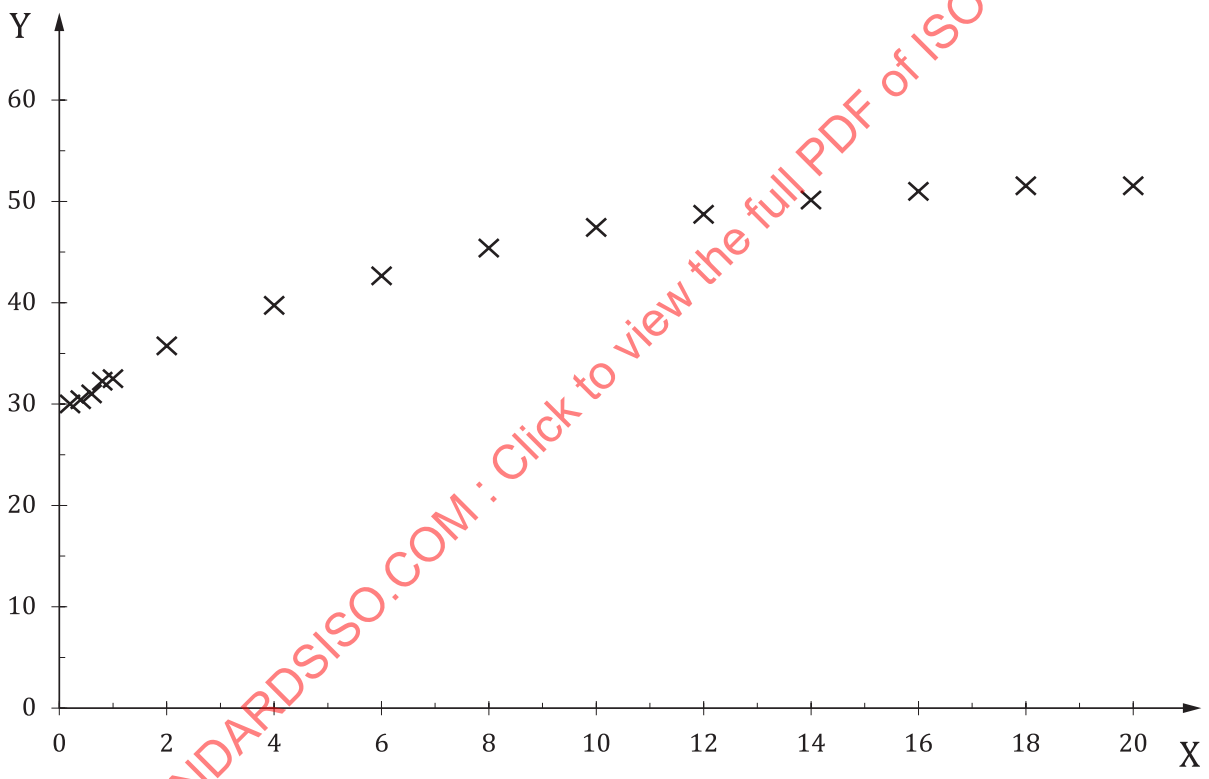
The next step is to plot E and $Q \times A$ for the different extents of reaction investigated. The plot of the E is seen in Figure C.4 and the plot of $Q \times A$ in Figure C.5.

Table C.2 — Kinetic parameters calculated for pellet P1

Specific total heat (J/g)	slope (–E/R)	E (kJ/mol)	*ln* $Q \times A$	$Q \times A$ *(J/(kg · s))*
0,2	3,61	30,01	11,73	1,24E+05
0,4	3,66	30,43	11,86	1,41E+05
0,6	3,73	31,01	12,10	1,80E+05
0,8	3,88	32,26	12,53	2,77E+05
1	3,91	32,51	12,60	2,97E+05

Table C.2 *(continued)*

Specific total heat (J/g)	slope (–E/R)	*E* (kJ/mol)	*ln Q×A*	*Q×A (J/(kg · s))*
2	4,30	35,75	13,57	7,82E+05
4	4,78	39,74	14,91	2,99E+06
6	5,13	42,65	15,76	6,99E+06
8	5,46	45,39	16,55	1,54E+07
10	5,71	47,44	17,12	2,72E+07
12	5,86	48,72	17,39	3,57E+07
14	6,03	50,13	17,73	5,01E+07
16	6,13	51,00	17,83	5,54E+07
18	6,20	51,55	17,80	5,38E+07
20	6,20	51,55	17,60	4,40E+07



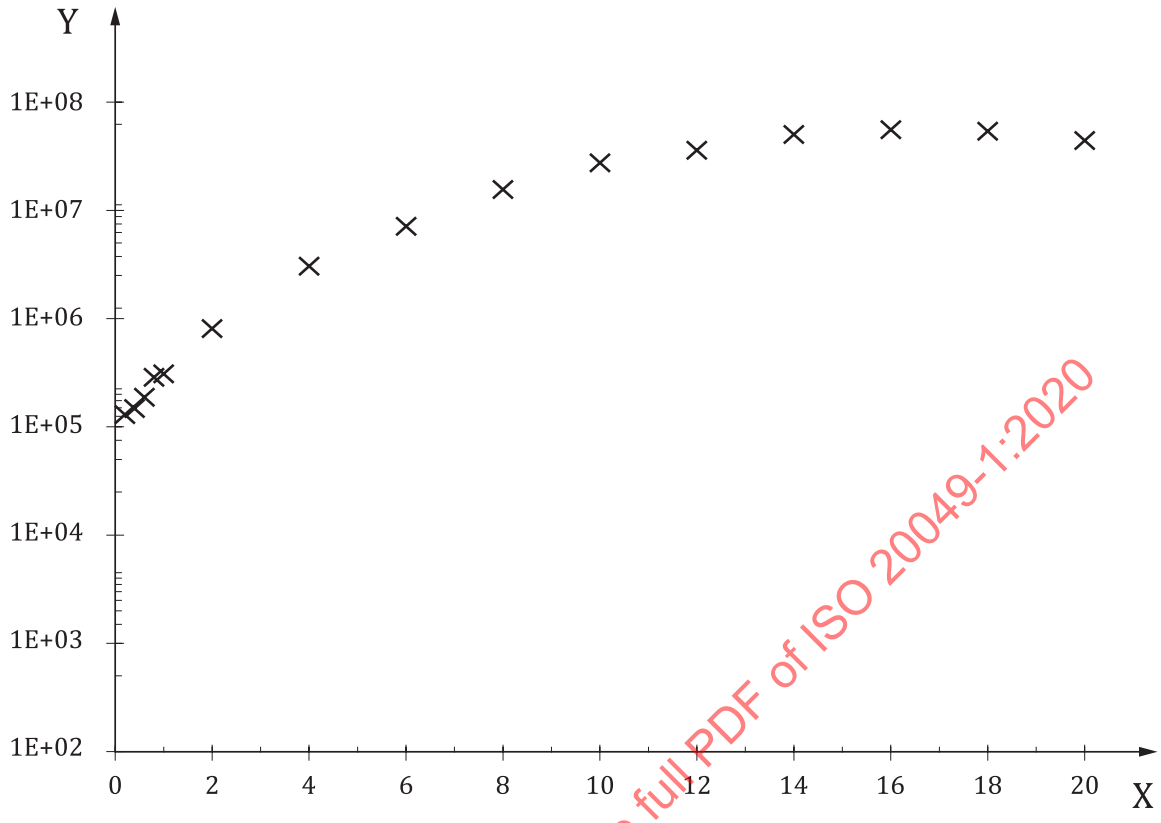
Key

Y activation energy (kJ/mol)

X specific total heat (J/g)

× Ea_2g

Figure C.4 — Plot of E_a versus specific total heat (J/g) for pellet P1



Key

Y log10 QA (J/kg·s) or (W/kg)

X specific total heat (J/g)

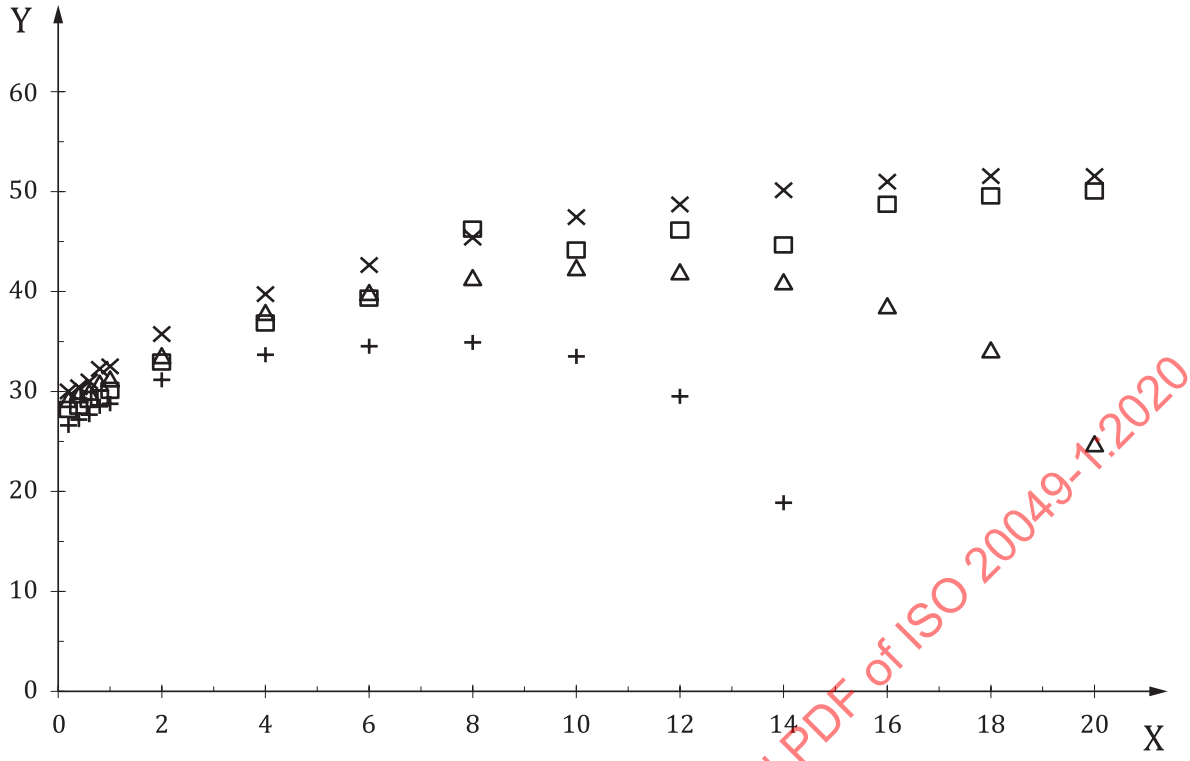
× QA_2g

Figure C.5 — Plot of $Q \times A$ versus specific total heat (J/g) for pellet P1

The magnitude of the kinetic parameters changes gradually with the extent of the reaction for the tests with P1 with 2 g of sample mass, especially for $Q \times A$, as can be seen from the plots of E (Figure C.4) and $Q \times A$ (Figure C.5). Note the logarithmic scale in the plot of $Q \times A$.

The effect of a too high sample mass-volume ratio is shown in Figure C.6. In this figure data on E is included for tests with P1 with 1 g, 3 g and 4 g sample mass loading in addition to 2 g. Figure C.6 shows that for larger mass-volume ratio the calculation of kinetic parameters (here E) becomes invalid.

The magnitude of the kinetic parameters will change with gradually reduction in both "fuel" and oxygen availability. The extent of these effects depends on the reactivity of the material tested, the temperature of the test, and the sample mass to air volume ratio.



Key

Y	activation energy (kJ/mol)
X	specific total heat (J/g)
□	Ea_1g
×	Ea_2g
△	Ea_3g
+	Ea_4g

Figure C.6 — Plot of *E* versus specific total heat (J/g) for pellet P1 for tests with different sample mass loadings

Annex D
(informative)

Information on the Interlaboratory study (ILS)

D.1 Introduction

An interlaboratory study (ILS) was held during the years 2017-2019 with nine participating laboratories. Laboratories from Canada, Germany, Norway and Sweden participated.

The ILS was made with three different types of wood pellets, all sampled at producers in Sweden. The pellets samples were stored at the site of the ILS-leader before sending out samples to the participating laboratories. The samples were stored in a freezer prior to shipping to the laboratories and shipping was prepared according to the instructions in this document.

Important knowledge on the influence on storing/shipping conditions gained during the ILS are presented in D.2.

Pellet P1 was first distributed and verification measurements of the test procedure were made. After adjusting the test procedure to the final procedure, P1 was sent out again to the participating laboratories for measurement. These are the results on measurement uncertainty for P1 presented in D.3.

After evaluating the results from the tests with P1 from the second test round, additionally two types of pellets, P2 and P3, were sent to the laboratories for measurement. The results on measurement uncertainty for pellets P2 and P3 are presented in D.3.

Information on the pellets tested in the ILS are given in Table D.1.

Table D.1 — Information on the pellets tested in the ILS

Pellet	Description	Moisture content[a] Weight-%
P1	Producer A 79,9 % spruce 20,1 % pine All dried before pelletizing using drum dryer	7,6
P2	Producer B 100 % pine All dried before pelletizing using drum dryer	8,8
P3	Producer B 100 % pine 50 % dried using drum dryer and 50 % dried using mechanical press	4,9

[a] Measured after production.

D.2 Influence of sample storage condition

When sending out pellet P1 for the second test round to the ILS participants, all packages with samples were delayed for 1 week in the postal handling. It was later seen that q_{max} was significantly lower compared with the results from the first test round. A test program was then established and conducted