International Standard

ISO 22207

First edition
2024-09

Kraft lignin — Determination of thermal stability by thermogravimetry

Thiolignine — Détermination de la stabilité thermique par thermogravimétrie

Reference number
ISO 22207:2024(en)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

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 document 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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 CSA (as CSA W207:20) and drafted in accordance with its editorial rules. It was assigned to Technical Committee(s) ISO/TC 6, *Paper, board and pulps*, and adopted under the “fast-track procedure”.

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

Lignin exists naturally in plants and trees and is one of the main components in wood. Given its abundance and its aromatic structure, lignin has the potential to replace fossil-based starting materials in a range of products including polymeric materials and fine chemicals. It is currently being evaluated by companies around the world as an alternative to petroleum-based chemicals for products such as carbon fibres, flavour and pharmaceutical ingredients, resins, foams, rubber additives, and thermoplastics.

The majority of world commerce is governed by regulations-based product standards. An absence of standards for products and properties therefore limits market access. With international interest and ongoing work in developing and commercializing new products from lignin, a strong knowledge of the physicochemical properties of lignin including chemical structure, molecular weight distribution, and thermal properties is required.

Thermal stability is crucial when targeting applications where lignin and other materials are processed at high temperatures. The present method aims to provide a standardized method to characterize the thermal stability of lignin in view of its use in applications requiring high temperatures. It will provide lignin producers and manufacturers an advantage to improve access to the lignin and lignin derivatives marketplaces globally.

Kraft lignin — Determination of thermal stability by thermogravimetry

1 Scope

This document describes the thermal analysis of kraft lignin using thermogravimetric methods.

Thermogravimetry can be used to determine the initial decomposition temperature(s), rate(s) of decomposition, and the temperature at maximum decomposition of various materials, including lignins at atmospheric pressure. All these temperatures are solely based on the mass loss and are not necessarily the real decomposition temperatures, because not all decompositions can generate evaporation at atmospheric pressure. Thus, these values are only for comparison purposes.

This procedure is applicable to solid lignins (e.g., powdered form) isolated using different isolation techniques (e.g., acidification with hydrochloric acid, sulphuric acid, etc., and carbonation using gaseous carbon dioxide) from the spent liquor (black liquor) generated in the kraft pulping process. It does not apply to raw black liquor.

Thermogravimetric measurement may be performed under different types of atmosphere, e.g., an inert atmosphere or an oxidative atmosphere.

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 4582:2017, *Plastics — Determination of changes in colour and variations in properties after exposure to glass-filtered solar radiation, natural weathering or laboratory radiation sources*

ISO/TS 24498:2022, *Paper, board and pulps — Estimation of uncertainty for test methods by interlaboratory comparisons*

3 Terms and definitions

For the purpose of this document, the following terms and definitions apply.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
decomposition temperature
temperature at which a substance chemically decomposes and the decomposed substance is able to evaporate at atmospheric pressure during the test

Note 1 to entry Td2% refers to the temperature at which decomposition led to a loss of 2% of the initial sample mass, and similarly Td5% and Td10% refer to the temperature at which decomposition led to a loss of 5 and 10% of the initial sample mass, respectively.

3.2
kraft lignin
depolymerized and chemically modified lignin isolated from a kraft pulping process, such as that originating from kraft black liquor sample

3.3
laboratory sample
total quantity of a type of material from a unique batch, available for testing and evaluation [prepared from a specific source using a specific procedure (e.g., a hardwood kraft lignin)]. It must be representative of the batch

3.4
lignin
class of complex, organic macromolecules, containing aromatic sub-units, that play a key role in the formation of cell walls in wood and bark, conferring mechanical strength and rigidity to the cell walls and to plants as a whole. Lignin is the main non-carbohydrate constituent of wood

3.5
replicate specimens
identical pieces of test material being evaluated which are all exposed, conditioned, and tested at the same time

3.6
test sample
portion of material taken from the laboratory sample after, for example, homogenizing, which is then prepared for testing or evaluation

3.7
test specimen
specific portion of the material upon which the testing is being performed

4 Principle

TG measurements are performed under an inert or oxidative atmosphere by heating a test specimen at a given rate up to a temperature of no more than 800 °C and monitoring the variation in mass as a function of temperature. Mass changes are indicators of thermal instability of the tested lignin; they are usually indicative of decomposition or oxidation reactions that form volatile substances during the test, as well as volatilization of components presented in the original sample. The change in mass is recorded as a TGA curve. Temperatures of decomposition (T_d) corresponding to specific mass losses, e.g., 2%, 5% and 10%, are determined from the curve (or raw data). The temperature of maximum decomposition rate is obtained from the first derivative of the TGA curve, i.e. the DTG curve.

5 Apparatus

The following apparatus shall be used for this protocol:

5.1 Thermobalance

Thermobalance that is able to generate heating and cooling at constant rates, able to generate constant purge gas flows, able to maintain test specimen at constant temperature and to measure temperatures and mass changes with an accuracy of 2 °C and 20 µg, respectively.

5.2 Pans inert to the test sample

Platinum pans.

5.3 Analytical balance

Analytical balance accurate to 0.01 mg.

5.4 Desiccator

Desiccator using Drierite™ or equivalent desiccant.

5.5 Drying oven

Drying oven with temperature control of (105 ± 2) °C.

5.6 Oxidative purge gas

Gas such as dry air, with a water content of less than 0,001% (w/w).

5.7 Inert purge gas

Gas such as helium, nitrogen or other inert purge gas, with an oxygen content of 0,001% (v/v) or less and a water content of less than 0,001% (w/w).

6 Sampling and test sample preparation

All samples and specimens shall be stored in a room-temperature desiccator at all times when not in use.

The test sample (1 g to 3 g) shall be representative of the laboratory sample.

The operator shall:

a) Air-dry the lignin at ambient conditions until it reaches sufficient dryness to allow grinding if the initial lignin moisture content is too high for it to be ground;

b) Gently grind the laboratory sample using mortar and pestle to homogenize the sample to a uniform powder;

c) Sieve the powder through a 200-mesh screen to ensure homogeneity;

d) Dry the test sample [1 g to 3 g of 200-mesh (P200) lignin powder] in an oven at (105 ± 2) °C until constant weight is reached; and

e) Cool to room temperature in a desiccator.

NOTE If a non-convection oven is used, make sure that the sample temperature is at 105 °C when it is in the oven.

7 Test specimen preparation

The operator shall:

a) Weigh an empty pan, record the mass, and tare the balance;

b) Add 5 mg to 15 mg of test sample to the pan ensuring that the minimum amount of material needed to completely cover the bottom of the pan is used. The pan must not be filled up to the top;

c) Record the mass of the test specimen; and

d) Ensure that the outer surface of the pan is clean and not contaminated with material.

8 Calibration

The operator shall calibrate the thermobalance according to the manufacturer's instructions.

9 Procedure

9.1 Cleaning Cycle

The operator shall run a cleaning cycle of the TGA instrument before starting a new batch of lignin samples to avoid contamination from previous samples.

9.2 Analysis method

The entire procedure shall be carried out on at least three replicate specimens, as follows:

a) Select the gas (e.g., air or N_2 for oxidative or inert conditions, respectively) and use an appropriate gas flow rate (e.g., 30 mL/min). In case there is a concern about the volatiles not being removed, apply vacuum line at the exhaust of the instrument.

b) Start the measurement program and record the TG and DTG curves. Heat the specimen under a flow of air or inert gas at a heating rate of 10 °C/min as follows:

   a. From room temperature to 105 °C;

   b. Set the weight at this point to 100%;

   c. Hold at 105 °C for 30 min; and

   d. From 105 °C to the maximum temperature allowed by the equipment, without exceeding 800 °C since the boiling point of sodium is 882,8 °C.

NOTE Other heating rates may be used, but must be reported.

10 Determination of decomposition temperatures ($T_{d2\%}$, $T_{d5\%}$ and $T_{d10\%}$), residue, and temperature of maximum decomposition rate

The dry mass after heating in the TGA at 105 °C shall be used as the initial mass for the calculation.

From the TG curve obtained under either oxidative or inert atmosphere (see Figure 1 for an example), determine $T_{d2\%}$, $T_{d5\%}$, and $T_{d10\%}$, where:

- $T_{d2\%}$ corresponds to the temperature at which a 2% mass loss or a 98% remaining mass is observed under the selected atmosphere.
- $T_{d5\%}$ corresponds to the temperature at which a 5% mass loss or a 95% remaining mass is observed under the selected atmosphere.
- $T_{d10\%}$ corresponds to the temperature at which a 10% mass loss or a 90% remaining mass is observed under the selected atmosphere.

Alternatively, raw data may be used to extract the values of decomposition temperatures by interpolation between the two points surrounding each target decomposition percentage.

From the TG curve expressed in %, determine the percentage of sample remaining at the end of the experiment under the selected atmosphere. This percentage corresponds to the amount of residue (expressed in %) obtained under the selected atmosphere.

From the TG curve expressed in mg, calculate the amount of residue remaining at the end of the measurement (expressed in %), as follows:

$$\%r = \left({}^{m_f}/_{m_i}\right) \times 100 \quad (1)$$

where m_i and m_f are the mass of sample measured at the initial (after heating at 105 °C) and final stages of the testing, respectively.

From the DTG curve obtained under either oxidative or inert atmosphere (see Figure 1 for an example), determine the temperature corresponding to the maximum change in mass with respect to temperature (change in mass/change in temperature).

Report the mean values of three determinations (of three different test specimens) for each laboratory sample. Temperatures are reported to the nearest integer.

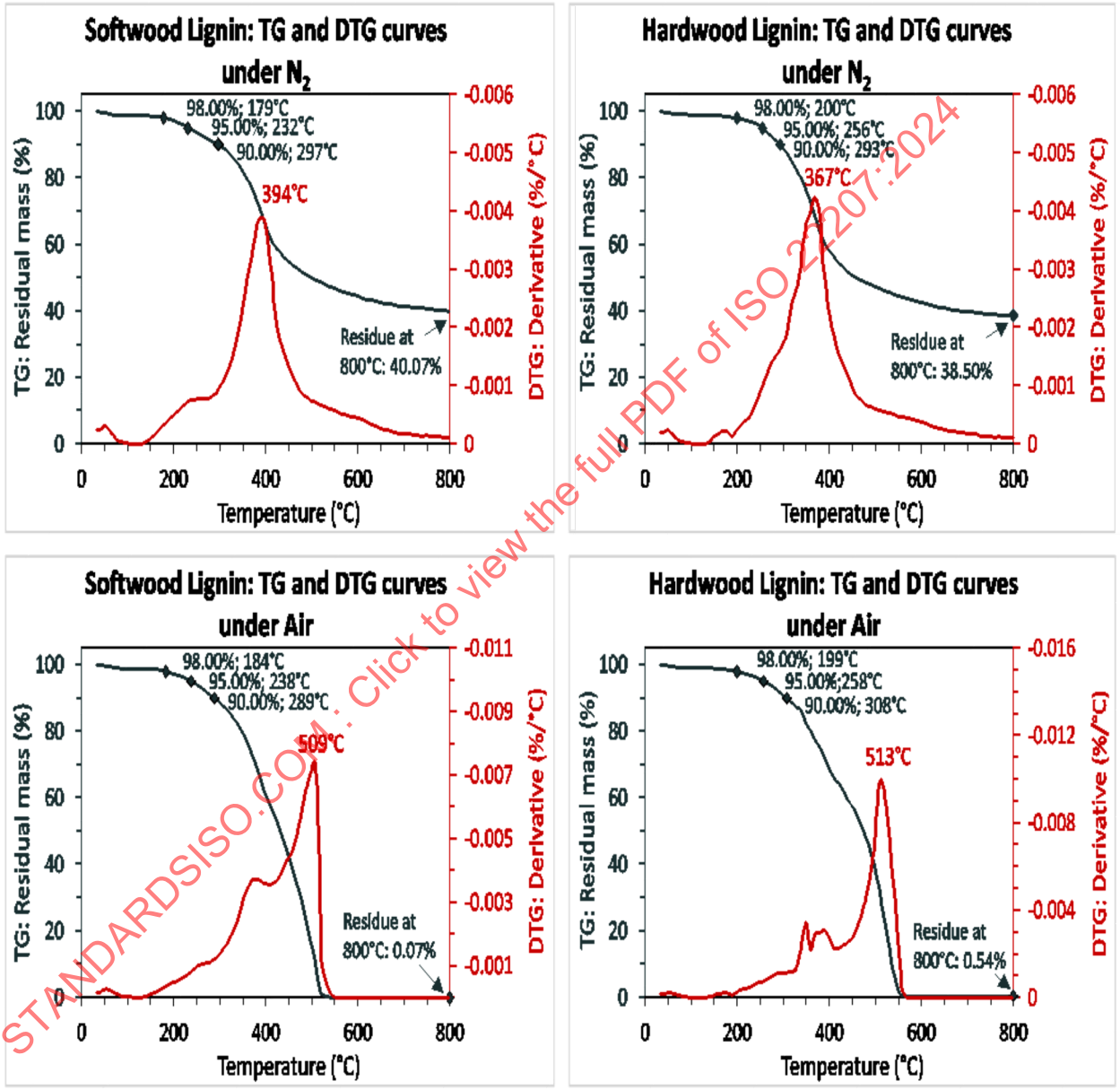

Figure 1 — Examples of TG and DTG curves obtained for kraft softwood and hardwood lignin samples (without extra drying at 105 °C) (See clause 10).

11 Test Report

The test report shall include the following information:

a) a reference to this test method;

b) the date and place of testing;

c) the complete identification of sample material tested;

d) the mass of test specimen;

e) the description of thermobalance used for the test (Q5000 IR model, TA instruments);

f) the specimen holder size and material;

g) the atmosphere and gas flow rate used (30 mL/min);

h) the rate of temperature increase (10 °C/min);

i) the temperature at which the mass calibration was carried out;

j) the material used for temperature calibration;

k) the TG and DTG curves;

l) the decomposition temperatures corresponding to 2%, 5%, and 10% mass loss in °C, and the standard deviations in °C;

m) the percentage of residue remaining at the end of the testing, and the standard deviation;

n) the temperature of maximum decomposition rate in °C, and the standard deviations in °C; and

o) information regarding any deviation from the standard procedures described in this test method and/or any other circumstances that might have affected the result.

Annex A
(informative)

Precision – Results of the round robin study

NOTE This Annex is not a mandatory part of this document.

In 2019, a round robin test was performed. Three samples, two softwood lignins and one hardwood lignin isolated from kraft black liquor, were used to determine the repeatability and reproducibility of this test method. Results from six national and international laboratories are given in Tables A.1 to A.7.

The calculations were made according to ISO/TS 24498.

The repeatability and reproducibility limits reported are estimates of the maximum difference which would be expected in 19 of 20 instances, when comparing test results for material similar to those described under similar test conditions. These estimates may not be valid for different materials or different test conditions.

NOTE Repeatability and reproducibility limits are calculated by multiplying the repeatability and reproducibility standard deviations by 2.77, where $2.77 = 1.96\sqrt{2}$.

Table A.1 — Temperature (°C) at 2% loss in inert atmosphere (N_2)

Sample	Number of laboratories	Grand mean value of Td at 2% loss	Repeatability standard deviation, *Sr* (°C)	Repeatability limit, *r* (°C)	Reproducibility standard deviation, *SR* (°C)	Reproducibility limit, *R* (°C)
SW-1	6	179	2.5	6.9	19.5	54.0
SW-2	6	173	2.5	6.9	15.2	42.1
HW-1	6	189	3.1	8.6	24.9	69.0

Table A.2 — Temperature (°C) at 5% loss in inert atmosphere

Sample	Number of laboratories	Grand mean value of Td at 5% loss	Repeatability standard deviation, *Sr* (°C)	Repeatability limit, *r* (°C)	Reproducibility standard deviation, *SR* (°C)	Reproducibility limit, *R* (°C)
SW-1	6	231	1.4	3.9	17.6	48.8
SW-2	6	237	1.8	5.0	14.4	39.9
HW-1	6	251	2.3	6.4	12.8	35.5

Table A.3 — Temperature (°C) at 10% loss in inert atmosphere (N_2)

Sample	Number of laboratories	Grand mean value of Td at 10% loss	Repeatability standard deviation, *Sr* (°C)	Repeatability limit, *r* (°C)	Reproducibility standard deviation, *SR* (°C)	Reproducibility limit, *R* (°C)