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This Test Method may include safety precautions which are believed to be appropriate at the time of publication of the method. The intent of these is to alert the user of the method to safety issues related to such use. The user is responsible for determining that the safety precautions are complete and are appropriate to their use of the method, and for ensuring that suitable safety practices have not changed since publication of the method. This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this method, the user must determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Gross heating value of black liquor

1. Scope

1.1 This method determines the gross (or high) heating value of black liquor, containing up to 55% by mass of water, derived from sodium-based kraft pulping¹.

1.2 The products of combustion in the recovery furnace are different from the bomb calorimeter products because of the reducing atmosphere which exists in the hearth zone of the furnace. A “heat of reaction correction” based on an elemental analysis of the waste liquor sample should be used to account for this difference. It is described in a TAPPI Steam and Power Committee Technical Information Sheet for calculation of recovery unit performance (TIP 0416-01 “Recovery Boiler Performance Calculation - Short Form”).

2. Summary

The gross heating value is measured for combustion in an adiabatic or isoperibolic oxygen bomb calorimeter. Complete combustion is ensured by the use of an auxiliary fuel, benzoic acid, to overcome the damping effect of the water in the specimen. The calorimeter water equivalent is determined by calibration with benzoic acid. Detailed procedures are given for carrying out the test and for calculating the gross heating value from the experimental data.

3. Significance

An accurate measure of the gross heating value of black liquor fed as fuel to recovery boilers is essential to determine the performance and operational efficiency of such boilers².

¹ Can also be used on spent liquors from NSSC and sodium sulfite pulping processes.

² This method was prepared in cooperation with the Steam and Power Committee. The gross heating value is used in their combustion calculations for recovery boiler performance and operational efficiency.

Approved by the Standard Specific Interest Group for this Test Method



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4. Definitions and units

4.1 The energy units as used in this method are defined as follows:

4.1.1 One Btu (British thermal unit) equals 1055.06 joules (J).

4.1.2 One Btu per pound equals 2.326 joules per gram (J/g).

4.1.3 One atmosphere equals 101.325 kPa.

4.2 The gross heating value is defined as the heat of combustion produced by complete oxidation of a liquor sample in an adiabatic or isoperibolic oxygen bomb calorimeter with all water in the combustion products remaining in liquid form. No correction is applied in the calculation of the gross heating value for the formation of nitric or sulfuric acids during the combustion of the sample. Such correction tests are very time consuming and generally reduce the calculated liquor heating value by less than 5%. For a typical black liquor containing 3 -5% sulfur (on dry black liquor solids), the correction for sulfuric acid formation would reduce the gross heating value by less than 20 J/o.d. gram or 0.15%.

5. Apparatus

5.1 Adiabatic or isoperibolic oxygen bomb calorimeter³ with bomb volume of about 400 mL with a calorimeter vessel of such size to enable assembled bomb to be completely submerged in water and a water jacket completely surrounding the calorimeter. The calorimeter stirrer should not produce a temperature rise greater than 0.01°C in a 10-min stirring period. The calorimeter jacket temperature must be quickly adjustable to that of the calorimeter during operation.

In adiabatic instruments, the temperature of the water in the surrounding jacket rises at the same rate as the temperature of the water in the bucket. In isoperibolic instruments, the jacket is maintained at a constant temperature as the temperature of the contents of the bomb rise. The isoperibolic calorimeter is highly automated and intended for use by laboratories which have a high demand for oxygen bomb calorimeter measurements. The isoperibolic bomb calorimeter is much more expensive than an adiabatic calorimeter, which is intended for laboratories which only occasionally need to determine the thermal heating value of samples. The precision of the isoperibolic calorimeter (about ± 0.15%) is also reportedly better than that for adiabatic calorimeters (about ± 0.30%). The procedure below is specific for an adiabatic bomb calorimeter although it and the calculations shown are applicable to both types of calorimeters.

5.2 *Thermometers:* (a) calorimeter bucket thermometer, certified as conforming to NBS specifications, 0.01°C subdivisions, with magnifier to estimate readings to 0.001°C; (b) jacket thermometer, 0.02°C subdivisions; and (c) room temperature thermometer, 0.1°C subdivisions.

5.3 *Specimen holder:* a stainless steel crucible is recommended, 25 mm diameter × 12 mm high, heated to remove any combustible material and cooled before use.

6. Calibration

6.1 Determine the water equivalent of the calorimeter as the average of a series of 10 individual runs with standard benzoic acid samples, made over a period of at least three days. The standard deviation should be 15.1 J/°C or less. Discard any individual run if there is evidence indicating incomplete combustion.

6.2 The mass of the benzoic acid pellet should be about 1.1 g. This mass yields about the same temperature rise (3°C) as an average liquor sample and benzoic acid mixture and conforms to the National Bureau of Standards (NBS) recommendation to use a mass of benzoic acid equal, in grams, to three times the volume of the bomb in liters. Make each calibration determination according to paragraphs 10.3, 10.4, 10.5, 10.6, and 10.7, and compute the corrected temperature rise, t , as shown in paragraph 11.1.

6.3 Following the directions outlined in paragraphs 11.2 and 11.3, determine the titration correction for nitric acid formation (e_1), the correction for the firing wire (e_2), and substitute into the following equation:

$$W = \frac{(H_B)(g_B) + e_1 + e_2}{t}$$

³ Names of suppliers of testing equipment and materials for this method may be found on the Test Equipment Suppliers list, available as part of the CD or printed set of Standards, or on the TAPPI website general Standards page

Where

W	=	water equivalent of calorimeter, J/°C
H_B	=	heat of combustion of benzoic acid, as stated in the NBS certificate, J/g of benzoic acid
g_B	=	mass of benzoic acid, g
t	=	corrected temperature rise, °C
e_1	=	titration correction for nitric acid formation, (J/g of N) (g of N/mL of Na_2CO_3) $\times$ mL Na_2CO_3 = 6 J/mL $\times$ mL of sodium carbonate solution required to neutralize the bomb washings
e_2	=	firing wire correction, (J/g of chromel C wire) (g of chromel C wire) = (5,862 J/g) $\times$ g of chromel C wire or (J/cm of chromel C wire) (cm of chromel C wire burned) = (9.755 J/cm) $\times$ cm of chromel C wire (see note 6 in Section 11.5)

Calibration tests should be repeated after changing any part of the calorimeter and periodically as a check on both calorimeter and operation technique.

7. Reagents and materials

7.1 *Firing wire*, No. 34 B & S gauge chromel C or equivalent, 100 ± 5 mm long between terminals. Platinum wire plus cotton thread may also be used in newer calorimeters.

7.2 *Oxygen gas*, minimum 99.5% O_2 .

7.3 *Alkali*, standard solution for titration of nitric acid in bomb washing from benzoic acid standardization. Dissolve 5.3 g of predried reagent grade, anhydrous sodium carbonate (Na_2CO_3) in distilled water, and dilute to 1000 mL. One mL of this solution is equivalent to the production of 6 J (see paragraph 11.2). This correction is used only in the benzoic acid standardization to determine the heat evolved by the formation of nitric acid due to the small amount of air, containing nitrogen, which was introduced during the loading of the combustion bomb.

7.4 *Benzoic acid*, NIST Standard Reference Material, calorimetric standard, pelletized before use. The heat of combustion (H_B) of the benzoic acid, J/g of benzoic acid, used in calibration or as auxiliary fuel, is listed in the NIST certificate issued with the acid⁴.

8. Safety

8.1 The mass of specimen and the pressure of the oxygen admitted to the bomb are not to exceed the bomb manufacturer's recommendations.

8.2 During ignition of a specimen, the operator must not permit any portion of his body to extend over the calorimeter.

8.3 Bomb parts are to be inspected carefully after each use. Threads on the main closure should be checked frequently for wear against a thread gage. The bomb should be returned after 500 firings to the manufacturer for inspection and possible proof firing.

8.4 The oxygen supply cylinder is equipped with a reducing valve, in addition to the needle valve and pressure gauge used in regulating the oxygen feed to the bomb. Valves, gauges and gaskets are required that meet industrial safety codes.

9. Sampling

Obtain a representative sample of black liquor, and store it properly by completely filling an alkali-resistant bottle. Black liquor is readily oxidized by atmospheric oxygen and will change composition even while stored in a completely filled and tightly sealed container. Accordingly, perform the analyses as soon as possible after sampling. Do not allow the sample or specimen to be exposed to the air more than necessary. Indicate in the analysis report if more than 24 h have elapsed between sampling and analysis.

⁴ Standard sample No. 39j.