

The calorific value of coal

Aims of the experiment

- To learn about coal as a fuel
- To determine the calorific value of coal
- To learn about calorimetry as a measurement method

Principles

Alongside mineral oil and natural gas, coal is one of the most important fossil energy sources. Coal is nothing other than a sedimentary rock that is brown to black in colour. It has been formed from plant remains over the course of several million years. The formation of coal can be mainly assigned to two geological periods, the tertiary period and the carboniferous period. During these periods, massive forest areas were flooded and isolated from the air, so that normal aerobic decay could no longer take place. A number of rocky layers covered the plant remains and through the resulting pressure and the high temperatures, coal was formed. This process is also known as coalification. The first stage of coalification is the formation of peat, then the formation of lignite followed by black coal. The furthest advanced stage of the coalification process is the formation of anthracite.

Coal has been used as a fuel for a long time. The heat of combustion is used for heating and for the production of electricity in power stations. Coal can also be used as a starting

point for all raw materials obtained from mineral oil. This requires the employment of various coal refinement methods, e.g. coking, gasification and hydrogenation of the coal.

The calorific value of coal can be determined with the help of calorimetric methods. The combustion takes place in a closed system, in which the entire heat energy can be recorded. The calorific value of a coal equivalent is used as a reference value for evaluating other fuels.

One kilogram of a coal equivalent corresponds to a quantity of energy of exactly 7000 kcal/kg. This is released when 1 kg of (hypothetical) coal is burned. This corresponds to 29.3076 MJ/kg.

In this experiment, the calorific value of coal is to be determined. For this, a double-walled glass apparatus is used as a calorimeter, which is filled with water and into which a stirrer and thermometer are immersed. The heat exchange between combustion gases and water is effected by a glass coil, so that the energy released can be completely transferred to the water. The temperature change of the water is then measured.

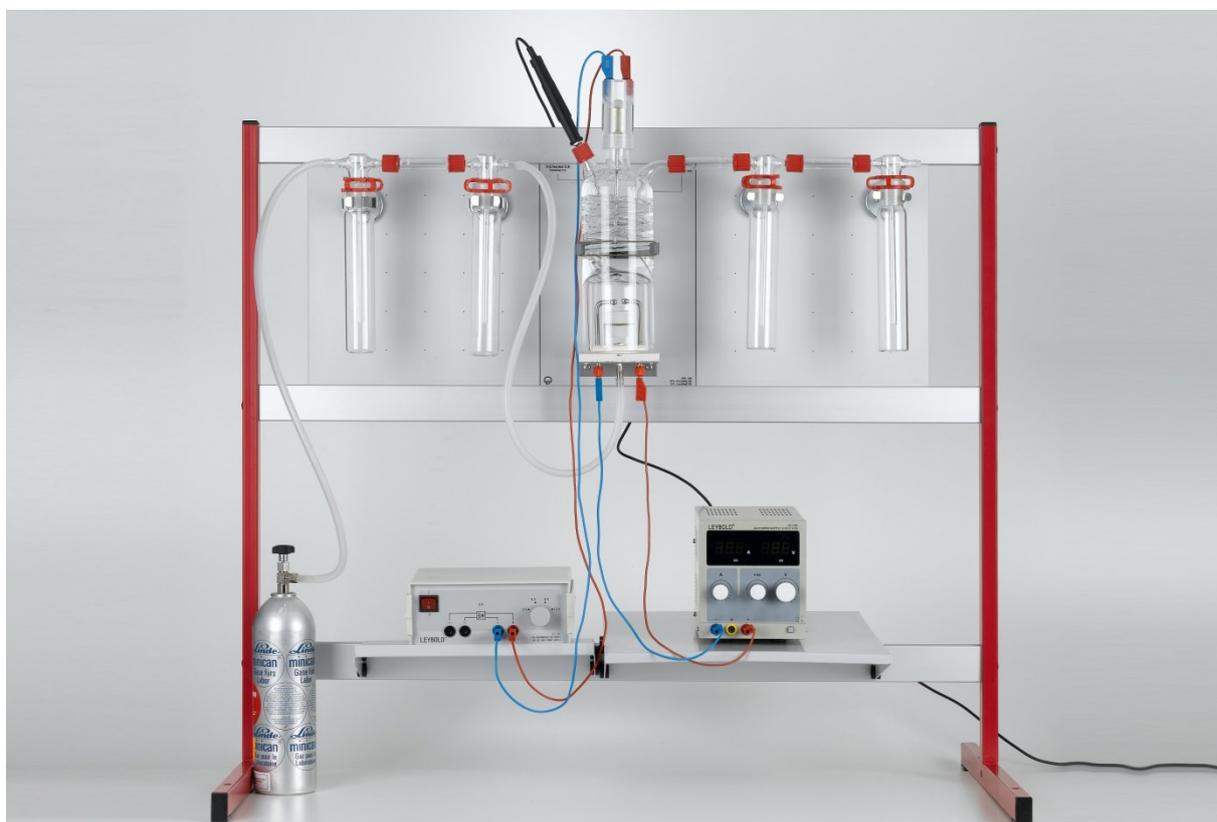


Fig. 1: Set-up of the experiment.

Risk assessment

Sodium hydroxide solution and sulphuric acid are corrosive substances. Wear protective clothing (lab coat, protective goggles). Fill the gas scrubbing bottles carefully and wear gloves to do this.

The experiment does not need to be performed in the fume cupboard as the combustion is controlled and the waste gases are also filtered out.

Please observe the instructions for use!

Sodium hydroxide solution, 1 mol/L	
	<p>Hazard statements</p> <p>H314 Causes severe skin burns and eye damage.</p> <p>Precautionary statements</p> <p>P280 Wear protective gloves/protective clothing/eye protection/face protection.</p> <p>P301 + P330 + P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.</p> <p>P305+P351+P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.</p>
<p>Signal word: Hazard</p>	
Sulphuric acid, conc.	
	<p>Hazard statements</p> <p>H314 Causes severe skin burns and eye damage.</p> <p>H290 May be corrosive to metals.</p> <p>Precautionary statements</p> <p>P280 Wear protective gloves/protective clothing/eye protection/face protection.</p> <p>P301+P330+P331 If swallowed: Rinse mouth. Do not induce vomiting.</p> <p>P309 If exposed or you feel unwell:</p> <p>P310 Immediately call a POISON CENTER or doctor/physician.</p> <p>P305+P351+P338 If in eyes: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.</p>
<p>Signal word: Hazard</p>	
Oxygen	
	<p>Hazard statements</p> <p>H270 May cause or intensify fire; oxidizer.</p> <p>H280 Contains gas under pressure; may explode if heated.</p> <p>Precautionary statements</p> <p>P244 Keep pressure reducer free of fat and oil.</p> <p>P220 Store away from combustible materials.</p> <p>P370+P376 In case of fire: Stop a leak if this can be done safely.</p> <p>P403 Store in a well ventilated place.</p>
	
<p>Signal word: Hazard</p>	

Equipment and chemicals

1	Calorimeter for solids, CPS	666 429
1	Panel frame C100, two-level, for CPS	666 428
2	Adhesive magnetic board 300 mm	666 4660
4	Holder, magnetic, size 4, 27...29 mm	666 4664
1	Console	301 312
1	Equipment platform 350 mm	726 21
3	Glass connector, 2 x GL 18	667 312
1	Sensor-CASSY	524 013
1	CASSY Lab 2	524 220
1	Temperature probe NiCr-Ni, 1.5 mm	529 676
1	NiCr-Ni adapter S	524 0673
4	Gas scrubber bottle, lower section	664 800
4	Glass tube insert with straight handle	664 805
4	Joint clip, from set of 10	665 392ET10
1	DC power supply 0...16 V/0...5 A	521 546
1	Low-voltage variable power supply	521 231
1	Stirring top with GL32 screw thread	666 819
3	Connecting leads 19 A, 50 cm, pair	501 45
1	Rubber tubing 8 mm diam., 1 m	667 180
1	Silicone tube 4 mm diam., 1 m	667 197
1	Connector, straight, 4 ... 15 mm diam.	604 510
1	Mortar, 70 mm diam.	667 092
1	Pestle, length 52 mm	608 360
1	Compact balance, 3000 g : 0.1 g	ADAHCB3001
1	Compact balance, 200 g : 0.01 g	667 7977
1	Fine regulating valve for Minican cans	660 980
1	Minican pressurised gas can, oxygen	660 998
1	Sodium hydroxide solution 1 mol/L, 500 mL	673 8420
1	Sulphuric acid, 95-98 %, 250 mL	674 7850
1	Anthracite coal, pieces, 100 g	674 9340
1	Stopcock grease	661 082

Also required:
PC with Windows XP/Vista/7/8
Small screwdriver (cross-head)

Set-up and preparation of the experiment

Set up the apparatus in accordance with Figure 1. Attach two gas scrubbing bottles in each case in front of and behind the calorimeter. Each of the bottles on the left serves as an empty safety bottle. Each of the bottles on the right is filled with liquids for cleaning the gases. The oxygen is passed through conc. sulphuric acid to remove the water. The waste gases are passed through sodium hydroxide solution to absorb the resulting CO₂.

Construction of the apparatus

1. Set up the CPS apparatus as shown in Figure 1.
2. Place the glass vessel of the calorimeter onto the base plate of the CPS panel. It closes with a rubber sponge seal.

Note: Apply a little stopcock grease onto the rubber sponge seal. This prevents any gas exchange between the internal space and the atmosphere, also in the case of larger pressure fluctuations.

The experiment can also be set up using stand materials. (see C 4.3.3.1)

Preparation of the gas line

1. Screw the fine regulating valve onto the oxygen gas bottle. Connect the valve to narrower tubing connected to wider tubing using a tube connector, then connect the wider tubing to the first gas scrubber bottle. Here, the glass tube of the gas scrubber bottle must point in the direction of the second gas scrubber bottle.
2. Connect the first gas scrubber bottle to the second gas scrubber bottle using a glass connector.

3. Pour sulphuric acid into the second gas scrubber bottle to a depth of about 3 cm. The sulphuric acid is used to dry the oxygen gas. Connect this scrubber bottle to the tube connector on the base plate of the calorimeter.

Caution: Take care when pouring in the sulphuric acid. Wear gloves! Make sure in all events that the gas scrubber bottle is correctly connected, so that the wash fluid is not drawn upwards into the gas stream.

4. The third gas scrubbing bottle remains empty. Pour sodium hydroxide solution into the fourth wash bottle up to around 3 cm high. Connect the third bottle to the tube connector at the top of the calorimeter using a glass connector. Here, the glass tube of the gas scrubbing bottle must point in the direction of the fourth gas scrubbing bottle.

Caution: Take care when pouring in the sodium hydroxide solution. Wear gloves! In addition, make sure in all events that the gas scrubbing bottle is correctly connected, so that the wash liquid is not drawn upwards into the gas stream.

5. Connect together the third and fourth scrubber bottles using a glass connector.

Preparation of the calorimeter

1. Weigh the glass vessel of the calorimeter whilst empty. Enter the value m (calorimeter vessel empty) into the table (see below). Pour water into the glass vessel and weigh again. Enter the value m (calorimeter vessel filled) into the table.

2. Place the glass vessel onto the base plate.

3. Insert the NiCr-Ni temperature probe into the calorimeter and connect it to the NiCr-Ni adapter S. Plug this into the Sensor-CASSY (Input A).

4. Screw the stirrer onto the thread of the calorimeter and connect to the low-voltage power supply with connecting leads (observe colour coding).

5. Bring the thermometer into a position where it is clear of the glass wall and there is sufficient separation to the stirrer.

Preparation of the sample

1. Place 1 or 2 pieces of coal into the mortar.

2. With the help of the pestle, crush the coal small in order to increase the surface area for igniting it and to ensure a better contact with the coiled filament.

3. Half fill the crucible with the crushed coal. Weight the filled crucible and enter the value m (crucible before the experiment) into the table.

4. Unscrew the coiled filament and insert the crucible into the holder.

5. Insert the coiled filament again so that it touches the powdered coal.

Performing the experiment

1. Load CASSY Lab settings.

2. For ignition, set a voltage of around 9 V and a current strength of 5mA on the DC power supply and switch off the power supply again until ignition.

Note: The power supply must not be connected to the calorimeter when setting the values.

3. Set the oxygen flow somewhat higher at the start, so that all of the apparatus is well filled. After about 30 seconds, set to a flow rate of 2 bubbles per second.

4. Now start recording the values in CASSY Lab 2 and switch on the stirrer.

5. Take the average value of the starting temperature after about 4 to 5 minutes as the starting value for the later calculations and enter it into the table (T_1). For this, in CASSY Lab choose  **Insert mean value** in the context menu.

6. The substance to be burned is ignited electrically. To do this, connect the calorimeter to the power supply with cables (see Fig. 1) and switch on the power supply.

7. The ignition time should be 5 - 10 seconds. Note the values for current I and voltage U . Afterwards, turn off the power supply. Obtain the time of ignition from the voltage diagram in CASSY Lab 2 and enter all values into the table.

8. After 5 minutes, switch off the oxygen flow, and after a further 5 minutes, stop the recording of the measurement values. Determine the end temperature T_2 again as an average over the last few minutes and enter this into the table.

9. As soon as the crucible has cooled down, remove it from the calorimeter vessel, weigh it and enter the value m (crucible after the experiment) in the table.

Observation

When an electric current flows through the coiled filament, it glows orange. After a short time, part of the coal will also begin to glow. However, this will extinguish when the oxygen flow is turned off. After the coal is extinguished, allow stirring of the water in the calorimeter to continue for at least a further 5 minutes until no further rise in temperature is observed.

Only a small amount of coal burns during the experiment.

Evaluation

The calorific value can be calculated from the temperature increase (see Fig. 2). For this, plot the starting temperature T_1 and the end temperature T_2 as mean values in the CASSY Lab data.

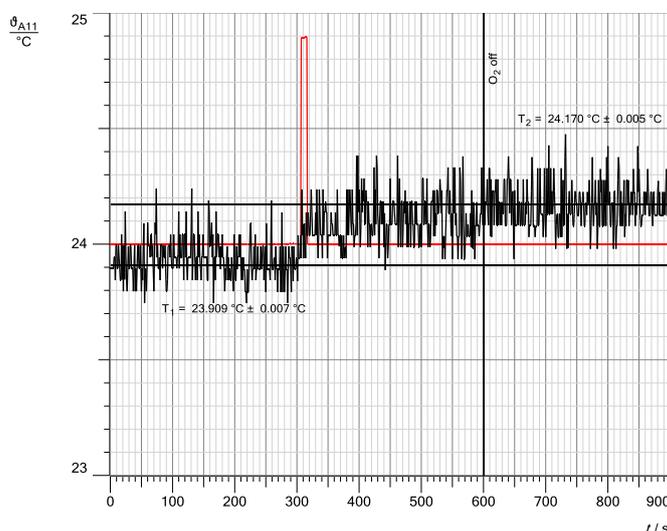


Fig. 2: Temperature and voltage measurements during the combustion of coal. Black: temperature, red: voltage.

The heat capacity of the calorimeter and the ignition energy introduced must be taken into account. All recorded values are compiled in Table 1.

Tab. 1: Recorded values during the experiment.

Required data	Values
m (crucible before the experiment)	20.21 g
m (crucible after the experiment)	20.19 g
m (burned coal)	0.02 g
Starting temperature T_1	23.91 °C
End temperature T_2	24.17 °C
Temperature difference ΔT	0.26 K
m (calorimeter vessel empty)	693.6 g
m (calorimeter vessel filled)	1391.2 g
m (water)	687.6 g
I_{ign}	4.6 A
U_{ign}	8.9 V
t_{ign}	10 s

Calculation of the specific heat capacity of the calorimeter $C_{\text{Calorimeter}}$

The calorimeter consists mainly of glass and water. All other components (stirrer, temperature probe) are not considered. The specific heat capacities for glass and water can be obtained from tables.

$$C_{\text{glass}} = 0.800 \text{ J/g}\cdot\text{K} \text{ and } C_{\text{water}} = 4.185 \text{ J/g}\cdot\text{K}$$

The heat capacity of the calorimeter $C_{\text{Calorimeter}}$ is calculated in simplified terms as the weighted sum of the heat capacities of glass and water.

$$\begin{aligned} C_{\text{Calorimeter}} &= m(\text{calorimeter empty}) \cdot C_{\text{glass}} + m(\text{water}) \cdot C_{\text{water}} \\ &= 693.6 \text{ g} \cdot 0.800 \text{ J/g}\cdot\text{K} + 687.6 \text{ g} \cdot 4.185 \text{ J/g}\cdot\text{K} \\ &= 3433 \text{ J/K} \end{aligned}$$

A thermal efficiency for the calorimeter of $\eta = 0.810$ was determined in calibration trials. This value was obtained from the Instructions for Use of the calorimeter and is a device-specific constant. This efficiency is offset against the heat capacity of the calorimeter. In this way, an effective heat capacity C_{eff} is obtained.

$$C_{\text{eff}} = \frac{C_{\text{Calorimeter}}}{\eta_{\text{Calorimeter}}} = \frac{3433 \text{ J/K}}{0.810} = 4238 \text{ J/K}$$

Calculation of the enthalpy of combustion of coal

The enthalpy of combustion is calculated using the following formula:

$$\begin{aligned} -\Delta H &= C_{\text{eff}} \cdot \Delta T \\ -\Delta H &= 4238 \frac{\text{J}}{\text{K}} \cdot 0.261 \text{ K} \\ -\Delta H &= 1106 \text{ J} \end{aligned}$$

The (introduced) ignition energy E_{ign} in joules is subtracted from this enthalpy of combustion. This is made up of voltage U , current I and ignition time t :

$$E_{\text{ign}} = U_{\text{ign}} \cdot I_{\text{ign}} \cdot t_{\text{ign}}$$

$$\begin{aligned} &= 8.9 \text{ V} \cdot 4.6 \text{ A} \cdot 10 \text{ s} \\ &= 409 \text{ J} \end{aligned}$$

The value for the ignition energy is subtracted from the enthalpy of reaction $-\Delta H$ previously calculated.

$$-\Delta H_{\text{corr}} = -\Delta H - E_{\text{ign}} = 1106 \text{ J} - 409 \text{ J} = 697 \text{ J}$$

Therefore, an energy of 697 J was released during the combustion of 25 mg of coal.

Calculation of the calorific value of coal

The enthalpy of reaction was corrected at all relevant values. The calorific value of the coal can now be calculated. This is the enthalpy of reaction $-\Delta H$ for a defined quantity, e.g. 1 g of coal.

$$\text{calorific value} = \frac{-\Delta H}{m(\text{burned coal})}$$

$$\text{calorific value} = \frac{697 \text{ J}}{0.02 \text{ g}}$$

$$\text{calorific value} = 34,9 \frac{\text{kJ}}{\text{g}} = 34,9 \frac{\text{MJ}}{\text{kg}}$$

The calorific value of this coal is 34.9 MJ/kg.

Result

In this experiment, the calorific value of coal was determined with the help of a calorimeter. Here, the calorimeter acts as a closed system in which the combustion takes place. A temperature increase results through burning in this system. The calorific value of the coal can then be calculated using this temperature difference.

The measured calorific value in the experiment can be compared with the calorific value known from the literature. The number of coal equivalents that the energy released in this experiment corresponds to can also be calculated. The calorific value obtained is 34.9 MJ/kg. This represents a discrepancy of 9 % compared with the literature value (approx. 32 MJ/kg), which is to be expected based on the method. This consists of heat loss through warming of the base plate and the incomplete transfer of heat from the combustion gas to the heat exchanger coil, as well as heat transfer from the calorimeter to the atmosphere and to the stand materials.

The calorific value of the coal used in the experiment is 34.9 MJ/kg. One coal equivalent corresponds to 29.3076 MJ/kg. The coal used in the experiment therefore corresponds to 1.2 coal equivalents.

The calorific value of other fuels can also be determined with this method.

Cleaning and disposal

The coal ash can be disposed of with the normal household waste. Unburned coal can be reused.

Sulphuric acid and sodium hydroxide solution can be stored in appropriately labelled containers for further experiments. If they are to be disposed of, neutralise if necessary and pour down the drain with plenty of water.