

The calorific value of fuel oil

Aims of the experiment

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

Principles

Heating oil is a liquid fuel consisting of carbon, hydrogen and a small amount of sulphur. Besides coal and natural gas, it is one of the most important means of heating. In the case of heating oil, we are dealing with a fossil fuel obtained during distillation from components of crude oil of low-flammability. The various types of heating oil that can be differentiated are: extra light, light, medium, heavy and extra heavy. Heating oils are classified according to increasing density, their ash and sulphur content and the ratio of carbon to hydrogen.

The standard heating oil used in households and in light industry is of the "extra light" type. It is ash-free and does not contain any incombustible components. It has, in addition, a high flash point of 55 °C. Therefore, it is very safe to store heating oil. Heating oil is obtained from crude oil by fractionated distillation. The crude oil is also heated to 400 °C in so-called tube furnaces. The major part of it evaporates immediately.

This vapour-liquid mixture arrives in the first distillation tower, in which normal pressure prevails. The evaporated fractions rise upwards, cool down and return to a liquid state on the various trays. They are separated according to their boiling points. The fractions thus obtained can be run off from the various trays. Heating oil is obtained from the fraction whose boiling point is around 250 - 380 °C.

In this experiment, the calorific value of heating oil is to be determined by calorimetry. To achieve this, heating oil will be burned in a calorimeter. This consists of a double-walled glass apparatus that is filled with water and into which a stirrer and thermometer are immersed. The heat exchange between the 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. Using this temperature change and the specific heat capacities of the substances involved, the calorific value can then be calculated using the formula $-\Delta H = C \cdot \Delta T$.






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 scrubber 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!

Sulphuric acid, conc.	
 <p>Signal word: Hazard</p>	<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>
Oxygen	
 <p>Signal word: Hazard</p>	<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 reduction valves free from grease 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>
Heating oil	
 <p>Signal word: Hazard</p>	<p>Hazard statements</p> <p>H226 Flammable liquid and vapour.</p> <p>H351 Suspected of causing cancer.</p> <p>H304 May be fatal if swallowed and enters the airways.</p> <p>H315 Causes skin irritation.</p> <p>H332 Harmful if inhaled.</p> <p>H373 Causes damage to organs through prolonged or repeated exposure.</p> <p>H411 Toxic to aquatic life with long-lasting effects.</p> <p>Precautionary statements</p> <p>P102 Keep out of reach of children.</p> <p>P301+P3310 IF SWALLOWED: Immediately call a POISON CENTER or doc-</p>

 <p>Signal word: Hazard</p>	<p>tor/physician.</p> <p>P331 Do NOT induce vomiting.</p> <p>P261 Avoid breathing vapour.</p> <p>P280 Wear protective gloves/protective clothing.</p> <p>P308+P313 IF exposed or concerned: Get medical advice/attention.</p> <p>P403+P233 Store in a well ventilated place. Keep container tightly closed.</p> <p>P273 Avoid release to the environment.</p>
Sodium hydroxide solution, 1 mol/L	
 <p>Signal word: Hazard</p>	<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>

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 212ET10
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	667 183
1	Silicone tubing 4 mm diam., 1 m	667 197
1	Connector, straight, 4 ... 15 mm diam.	604 510
1	Dropping pipette, 10 pcs.	665 953
1	Rubber bulbs for dropping pipette, 10 pcs.	665 954
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	Heating oil, 250 mL	672 1740
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 scrubber bottles before and two after the calorimeter. Each of the bottles on the left serves empty as a safety bottle. Each of the bottles on the right is filled with liquids for scrubbing 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 CO_2 .

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 is closed with a rubber sponge seal.

Note: Apply a little stopcock grease to the rubber sponge seal. This prevents an exchange of gases between the internal space and the atmosphere even 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 a piece of narrow tubing connected to a piece of 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 scrubber bottle however remains empty. Pour sodium hydroxide solution into the fourth gas scrubber bottle up to a depth of about 3 cm. 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 scrubber bottle must point in the direction of the fourth gas scrubber bottle.

Caution: Take care when pouring in the sodium hydroxide solution. Wear gloves! In addition, make sure in all events that the gas scrubber 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 around 40 drops of heating oil into the crucible using a dropping pipette.
2. Weigh the filled crucible and enter the value m (crucible before the experiment) into the table.
3. Unscrew the coiled filament and insert the crucible into the holder.
4. Re-insert the coiled filament so that it is just above the surface of the heating oil.

Performing the experiment

1. Load CASSY Lab settings.

2. For ignition, set a voltage of around 9 V and a current of 5 mA 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 the entire 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. The average value of the starting temperature after about 4 to 5 minutes is used as the starting value for the later calculations and entered 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 the cables (see Fig. 1) and switch on the power supply.
7. The ignition time should be 2 - 5 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. Switch off the oxygen flow after 5 minutes and stop recording the values after a further 5 minutes. 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. The heating oil then starts to burn immediately. This can start so suddenly that a small amount of the heating oil splashes out of the crucible. However, this flame will extinguish when the oxygen flow is turned off. After extinguishing the flame, the water in the calorimeter is stirred for at least a further 5 minutes until no further temperature increase is observed.

Evaluation

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

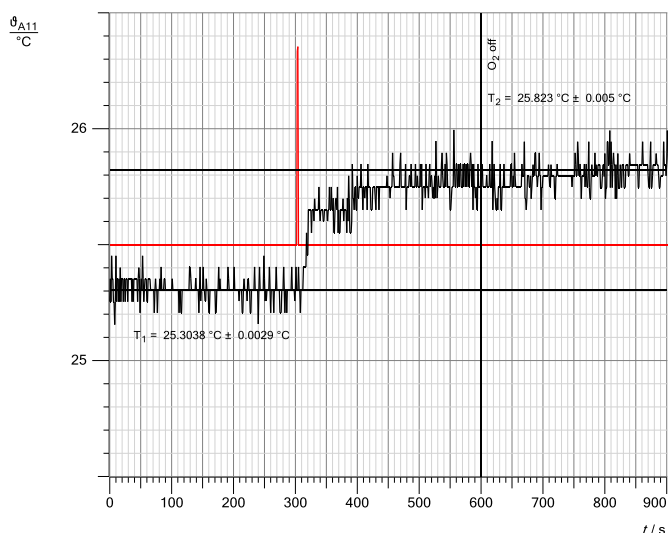


Fig. 2: Temperature and voltage measurements during the combustion of heating oil. Black: temperature, red: voltage.

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

Tab. 1: Values recorded during the experiment.

Required data	Values
m (crucible before the experiment)	19.97 g
m (crucible after the experiment)	19.92 g
m (heating oil burned)	0.05 g
Starting temperature T_1	25.30 °C
End temperature T_2	25.82 °C
Temperature difference ΔT	0.52 K
m (calorimeter vessel empty)	693.6 g
Required data	Values
m (calorimeter vessel filled)	1381.7 g
m (water)	688.1 g
I_{ign}	4.2 A
U_{ign}	8.5 V
t_{ign}	2 s

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

The calorimeter consists mainly of glass and water. No other components (stirrer, temperature probe) are 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.

$$\begin{aligned} C_{\text{Calorimeter}} &= m(\text{calorimeter empty}) \cdot c_{\text{glass}} + m(\text{water}) \cdot c_{\text{water}} \\ &= 693.6 \text{ g} \cdot 0.800 \text{ J/g} \cdot \text{K} + 688.1 \text{ g} \cdot 4.185 \text{ J/g} \cdot \text{K} \\ &= 3435 \text{ J/K} \end{aligned}$$

A thermal efficiency value 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. Thus an effective heat capacity of C_{eff} is obtained.

$$C_{\text{eff}} = \frac{C_{\text{calorimeter}}}{\eta_{\text{calorimeter}}} = \frac{3435 \text{ J/K}}{0.810} = 4241 \text{ J/K}$$

Calculation of the enthalpy of combustion of heating oil

The enthalpy of combustion is calculated using the following formula:

$$\begin{aligned} -\Delta H &= C_{\text{eff}} \cdot \Delta T \\ -\Delta H &= 4241 \frac{\text{J}}{\text{K}} \cdot 0.520 \text{ K} \\ -\Delta H &= 2205 \text{ J} \end{aligned}$$

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 :

$$\begin{aligned} E_{\text{ign}} &= U_{\text{ign}} \cdot I_{\text{ign}} \cdot t_{\text{ign}} \\ &= 8.5 \text{ V} \cdot 4.2 \text{ A} \cdot 2 \text{ s} \\ &= 71 \text{ J} \end{aligned}$$

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

$$-\Delta H_{\text{corr}} = -\Delta H - E_{\text{ign}} = 2205 \text{ J} - 71 \text{ J} = 2134 \text{ J}$$

Therefore, an energy of 2134 J was released during the combustion of 50 mg of heating oil.

Calculation of the calorific value of heating oil

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

$$\begin{aligned} \text{calorific value} &= \frac{-\Delta H}{m \text{ burned heating oil}} \\ \text{calorific value} &= \frac{2134 \text{ J}}{0.05 \text{ g}} \\ \text{calorific value} &= 42.7 \frac{\text{kJ}}{\text{g}} \end{aligned}$$

The calorific value of this heating oil is 42.7 kJ/g or 42.7 MJ/kg.

Result

In this experiment, the calorific value of heating oil 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 heating oil can then be calculated using this temperature difference.

The calorific value measured in the experiment can be compared with the calorific value known from the literature. The calorific value obtained is 42.7 MJ/kg. This represents a discrepancy of around 6% compared with the literature value (approx. 45.4 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. A further source of error arises if the heating oil ignites very spontaneously and, in so doing, splashes out of the crucible. Because of this, the mass of heating oil burned appears higher than it actually is.

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

Cleaning and disposal

Dispose of the remaining heating oil in the crucible in a container for liquid organic waste. It must not be emptied into drains under any circumstances. Then clean the crucible, preferably with acetone.

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.