# Determination of the Heating Value (Fuel Value) of Solid and Gaseous Fuels in a horizontal Calorimeter 

(Item No.: P3021301)

## Curricular Relevance

| Area of Expertise: Chemistry | Education Level: University | Chemistry | Experiment: <br> Determination of the Heating Value (Fuel Value) of Solid and Gaseous Fuels in a horizontal Calorimeter |
| :---: | :---: | :---: | :---: |
| Difficulty | Preparation Time | Execution Time | Recommended Group Size |
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| Intermediate | 10 Minutes | 10 Minutes | 2 Students |

## Additional Requirements:

- Mineral coal
- Brown coal
- Natural gas (from the gas supply)
- Cigarette lighter or matches


## Experiment Variations:

- Measurement by using Cobra4 hand-held pressure and temperature measuring instrument, Cobra4 Mobile-Link and PC with USB interface (Windows XP or higher)


## Keywords:

Heating Value, Fuel Value, Calorimeter

## Overview

## Short description

## Principle:

The heating value (energy value, calorific value) of a substance, is the amount of heat released during the combustion of a specified amount of it. The energy value is a characteristic for each substance. It is measured in units of energy per unit of the substance, usually mass, such as: $\mathrm{kJ} / \mathrm{kg}, \mathrm{kJ} / \mathrm{mol}, \mathrm{kcal} / \mathrm{kg}$, Btu/lb. Heating value is commonly determined by use of a bomb calorimeter.

## Note:

For the determination of the heating value of solid fuels (mineral coal, hard coal coke, brown coal, peat and wood) we will use 0.5 to 1 g pieces of commercially available materials. Wood and torf must be air-dried. Coal, coke and brown coal must be stored dry.

## Safety information:

The material glows brightly and burns rapidly in the stream of oxygen. Wear protective glasses so that you are not blinded.

## Safety instructions



## Important!

Wear protective glasses so that you are not blinded.
Never use acetylene in school experiments!

## Propane

H220: Extremely flammable gas.
H280: Contains gas under pressure; may explode if heated.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking. P381: Eliminate all ignition sources if safe to do so.

## n-butane

H220: Extremely flammable gas.
H280: Contains gas under pressure; may explode if heated.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking. P377: Leaking gas fire - do not extinguish unless leak can be stopped safely.

## Equipment

| Position No. | Material | Order No. | Quantity |
| :---: | :---: | :---: | :---: |
| 1 | Cobra4 hand-held pressure and temperature measuring instrument, Cobra4 Mobile-Link | 12736-01 | 1 |
| 2 | Gasometer 1000 ml | 40461-00 | 1 |
| 3 | Glass jacket | 02615-00 | 1 |
| 4 | Steel cylinder oxygen, 2 I, filled | 41778-00 | 1 |
| 5 | Calorimeter insert for glass jacket | 02615-01 | 1 |
| 6 | Support base DEMO | 02007-55 | 1 |
| 7 | Reducing valve f.oxygen | 33482-00 | 1 |
| 8 | Compressed gas, n-butane, 510 g | 41773-11 | 1 |
| 9 | Table stand for 2 I steel cylinders | 41774-00 | 1 |
| 10 | Combustion lance for gases | 02613-00 | 1 |
| 11 | Fine control valve | 33499-00 | 1 |
| 12 | Compressed gas, propane, 71 | 41772-10 | 1 |
| 13 | Butane burner, Labogaz 206 type | 32178-00 | 1 |
| 14 | Retort stand, $\mathrm{h}=750 \mathrm{~mm}$ | 37694-00 | 1 |
| 15 | Barrel base PHYWE | 02006-55 | 1 |
| 16 | Magnet, $\mathrm{d}=10 \mathrm{~mm}$, $\mathrm{l}=200 \mathrm{~mm}$ | 06311-00 | 1 |
| 17 | Test tube GL25/8, w.hose connec. | 36330-15 | 1 |
| 18 | Paper,ceram.fibre,1.0x500x2000mm | 38750-01 | 1 |
| 19 | Water jet pump, plastic | 02728-00 | 1 |
| 20 | Commercial weight, 1000 g | 44096-70 | 1 |
| 21 | Lab thermometer,w.stem, +15..+40C | 38057-00 | 2 |
| 22 | Glass tubes,right-angled, 10 | 36701-59 | 1 |
| 23 | Wrench for steel cylinders | 40322-00 | 1 |
| 24 | Universal clamp | 37715-00 | 5 |
| 25 | Scissors, straight, 180 mm | 64798-00 | 1 |
| 26 | Protective glasses, green glass | 39317-00 | 1 |
| 27 | Tweezers,straight,blunt, 200 mm | 40955-00 | 1 |
| 28 | Right angle clamp | 37697-00 | 4 |
| 29 | Support rod, stainless steel, $\mathrm{I}=250 \mathrm{~mm}, \mathrm{~d}=10 \mathrm{~mm}$ | 02031-00 | 2 |
| 30 | Funnel, glass, top dia. 55 mm | 34457-00 | 1 |
| 31 | Graduated vessel, 1 I, with handle | 36640-00 | 1 |
| 32 | Pinchcock, width 15 mm | 43631-15 | 1 |
| 33 | Silicone tubing i.d. 7 mm | 39296-00 | 3 |
| 34 | Magnetic stirring bar 30 mm , cylindrical | 46299-02 | 1 |
| 35 | Butane cartridge C206, without valve | 47535-01 | 1 |
| 36 | Hose clip, diam. 8-16 mm, 1 pc. | 40996-02 | 2 |
|  | Additional material: |  |  |
|  | Mineral coal (approx 1g) |  |  |
|  | Brown coal (approx 1g) |  |  |
|  | Coke (approx 1g) |  |  |
|  | Wood (approx 1g) |  |  |
|  | Turf / peat (approx 1g) |  |  |
|  | Natural gas (from the gas supply) |  |  |
|  | Cigarette lighter or matches |  |  |
|  | Alternative material (instead of Cobra4): |  |  |
|  | Thermometer, $-15 \ldots+40^{\circ} \mathrm{C}$ | 38057-00 | 2 |
|  | Digital barometer | 03099-00 | 1 |

## Task

1. Determination of the heating value of solid fuels
2. Determination of the heating value of gaseous fuels (natural gas, propane, butane)


## Set-up and procedure



Important! Wear protective glasses so that you are not blinded.

## 1. Determination of the heating value of solid fuels

Note: For the determination of the heating value of solid fuels (mineral coal, hard coal coke, brown coal, peat and wood) we will use 0.5 to 1 g pieces of commercially available materials. Wood and torf must be air-dried. Coal, coke and brown coal must be stored dry.

Set up the experiment as shown in Fig. 1. Mount the calorimeter insert (2) in the glass jacket (1) as explained in the instruction manual. Fix the assembled open calorimeter horizontallyon two short rods as shown in Fig 1. About 500 g of water must now be filled into the glass jacket by pouring it in through one of the two vertical screw cap adapters (funnel). As the exact mass of this water must be known, first fill about 500 ml of water into the graduated vessel and weigh this on the balance to determine the mass $\left(=m_{1}\right)$. Pour the water carefully into the jacket, without spillage, and re-weigh the graduated vessel $\left(=m_{2}\right)$. The difference in the!wo weighings gives the mass of water filled into the jacket ( $\left.m\left(\mathrm{H}_{2} \mathrm{O}\right)=m_{2}-m_{1}\right)$.

Slide a magnetic stirrer bar (length 30 mm ) into the glass jacket through one of the vertical adapters and fit the thermometers (scale division $0.1^{\circ} \mathrm{C}$ ) in the adapters. Connect a bubble counter (test tube with inlet tube and right-angled glass tube) containing only a liltle water to the outlet opening of the calorimeter. Connect a vacuum pump (water jet pump or membrane pump) to the bubble counter to allow air to be drawn through the calorimeter.
Fix a universal clamp vertically to the barrel base and use it to hold the combustion lance horizontally. Fix a butane canister on the short rod as shown in Fig. 1. This will be used to generate a very small ignition flame. Connect this canister to the combustion lance with silicone hose, and the combustion lance to a source of oxygen (steel cylinder) as shown in Fig. 1. The tubing can be connected to the butane burner by screwing off the top of the burner and pushing the tubing over the thread of the burner base. 80th ends of each tubing must be securely fastened with hose clips. Use an accurate balance to determine the mass of a prepared piece of one of the materials to be tested (about 0.5 to 1 g ). Place it on a strip of ceramic paper and slide
it weil into the combustion chamber of the calorimeter (see Fig. 1: $a=$ ceramic paper, $b=$ test sampie).
Using a bar magnet, move the magnetic stirrer bar back and forth in the water until both thermometers show the same temperature. Note this ( $=$ starting temperature $\vartheta_{1}$ ). Turn on the vacuum purnp and adjust it so that a sUfficiently strong current of air is sucked through the calorimeter. The strength of the air current can be seen in the bubble counter. This adjustrnent requires a liltle experience and can be made by means of a pinchcock fitted onto the tubing be!ween purnp and bubble counter. The air flow is necessary to ensure that all hot gases pass through the calorimeter.
Now adjust a small ignition flame at the end of the combustion lance as follows: Open the valve on the butane canister and the fine regulating valve of the combustion lance and adjust them to get a weak flow of gas. Ignite this at the mouth of the combustion lance and adjust the length of the flame to 1 to 2 cm .
Add oxygen to it so that a very small ignition flame of about 5 mm length results.
Quickly position this ignition flame in the calorimeter, so that it touches upon the piece of material under test, by moving the barrel base. The material ignites in a fraction of a second. When this occurs, immediately close the fine regulating valve so that no further combustion gas burns in the calorimeter, but that only oxygen continues to be fed through the combustion lance over the sampie.


## 2. Determination of the heating value of gaseous fuels (natural gas, propane, butane)

The set up is the same as in the first experiment, except that a 1000 ml gasometer is additionally fixed to the retort stand (Fig. 2).

Fill the gasometer with approximately 600 to 1000 ml of the gas to be tested (natural gas can be taken directly from the gas supply, propane and butane etc. from corresponding compressed gas canisters. Never use acetylene in school

## experiments!)

Adjust the scale of the gasometer, so that the standard volume of the stored gas is directly shown. This saves the need for conversion of measured values (see the instruction manual of the gasometer).
First determine the starting temperature $\vartheta_{1}$ of the calorimeter, as described above. Following this, turn on the vacuum pump and adjust it with aid of the pinchcock so that sufficient air is sucked through the calorimeter. Allow gas to slowly flow out of the gasometer through and out of the combustion lance, ignite it immediately and adjust the flame to a length of about 2 to 3 em. Add as much oxygen to the flame as is necessary for complete, i.e. soot-free, combustion.

Wait until the plunger of the gasometer moves down past a fixed scale value (e.g. 500 ml ) and exactly at this moment insert the combustion lance well into the combustion chamber of the calorimeter by moving the barrel base. Allow about 500 ml of natural gas (or 200 to 300 ml of propane or butane) to burn, keeping the water in the calorimeter in continual, gentle movement. Close the valve of the combustion lance, stop the flow of oxygen and of air, and keep stirring the water for about another half a minute until both thermometers show the same temperature (i.e. the same increase in temperature). Note this final temperature $\vartheta_{2}$. Read the norm volume $V_{0}$ of the combusted portion of gas from the gasometer scale.


## Results and evaluation

## 1. Determination of the heating value of solid fuels

## Observation:

The material glows brightly and burns rapidly in the stream of oxygen (Important! Wear protective glasses with dark-glass so that you are not blinded).

## Continuation:

During the combustion, gently agitate the water in the calorimeter to ensure that the liberated heat of combustion passes as completely as possible into the water. Stop the flow of air and of oxygen as soon as the combustion has finished. Agitate the water again briefly, until both thermometers show the same temperature. Read and note this final temperature $\left(\vartheta_{2}\right)$.

## Evaluation:

To calculate the amount of heat energy which was liberated, we need to know, in addition to the starting and final temperatures $\left(\vartheta_{1}\right)$ and $\left(\vartheta_{2}\right)$ the heat capacity of the calorimeter $C_{\text {cal }}$. This is on average $410 \mathrm{~J} / \mathrm{K}$ for the glass jacket calorimeter.
(Should you want to determine the heat capacity of the calorimeter to be used exactly, see the detailed description of the procedure in the instruction manual of the glass jacket).

Calculation of the heating value $H$ for coal from the values determined in an experiment:

Mass of coal burnt
Starting tenmprature of the calorimeter Final temperature of the calorimeter

Mass of water in the calorimeter Specific heat of water Heat capacity of the calorimeter

$$
\begin{aligned}
\vartheta_{1} & =0.34 \mathrm{~g} \\
\vartheta_{2} & =22.7^{\circ} \mathrm{C} \\
\Delta T & =27.5^{\circ} \mathrm{C} \\
m_{w} & =500 \mathrm{~K} \\
c_{w} & =4.1798 \mathrm{Jg}^{-1} \mathrm{~K}^{-1} \\
C_{\mathrm{cal}} & =410 \mathrm{~J} / \mathrm{K}
\end{aligned}
$$

$$
\begin{aligned}
H & =\frac{\left(m_{\mathrm{w}} \cdot c_{\mathrm{w}}+C_{\mathrm{cal}}\right) \cdot \Delta T}{m} \\
& =\frac{\left(500 \mathrm{~g} \cdot 4.1798 \mathrm{~J} \cdot \mathrm{~g}^{-1} \cdot \mathrm{~K}^{-1}+410 \mathrm{~J} \cdot \mathrm{~K}^{-1}\right) \cdot 4.8 \mathrm{~K}}{0.34 \mathrm{~g}} \\
& =35292.7 \frac{\mathrm{~J}}{\mathrm{~g}}=35.2927 \frac{\mathrm{~kJ}}{\mathrm{~g}} \\
& =35292.7 \frac{\mathrm{~kJ}}{\mathrm{~kg}}
\end{aligned}
$$

Note: According to the type of coal, the heating value can be a liltle higher or lower. It is on average $35700 \mathrm{~kJ} / \mathrm{kg}$.

## 2. Determination of the heating value of gaseous fuels (natural gas, propane, butane)

Galculate the heating value per $\mathrm{m}^{3}$ from the values determined in the experiment, as in the following example:

Volume of gas burnt

$$
\begin{aligned}
V_{0} & =0.390 \mathrm{I} \\
\vartheta_{1} & =23.1^{\circ} \mathrm{C} \\
\vartheta_{2} & =28.3^{\circ} \mathrm{C} \\
\Delta T & =5.2 \mathrm{~K}
\end{aligned}
$$

Starting temperature of the calorimeter $\vartheta_{1}=23.1^{\circ} \mathrm{C}$
Final temperature of the calorimeter $\quad \vartheta_{2}=28.3^{\circ} \mathrm{C}$

$$
\begin{aligned}
H & =\frac{\left(m_{\mathrm{w}} \cdot c_{\mathrm{w}}+C_{\mathrm{cal}}\right) \cdot \Delta T}{V_{0}} \\
& =\frac{\left(500 \mathrm{~g} \cdot 4.1798 \mathrm{~J} \cdot \mathrm{~g}^{-1} \cdot \mathrm{~K}^{-1}+410 \mathrm{~J} \cdot \mathrm{~K}^{-1}\right) \cdot 5.2 \mathrm{~K}}{0.3091} \\
& =33332.0 \frac{\mathrm{~J}}{\mathrm{l}}=33332 \frac{\mathrm{~kJ}}{\mathrm{~m}^{3}}
\end{aligned}
$$

Note: As the composition of natural gas can vary somewhat, the value measured can also vary. Pure methane has an upper heating value $H_{\mathrm{u}}$ of $39800 \mathrm{~kJ} / \mathrm{m}^{3}$ and a lower heating value $H_{\mathrm{l}}$ of $35800 \mathrm{~kJ} / \mathrm{m}^{3}$.

## Remarks:

The determination of heating values in the glass jacket calorimeter gives quite good results when the value for $\Delta T$ is not allowed to go above about 6 K . When the difference between $\vartheta_{1}$ and $\vartheta_{2}$ is higherthan this, some heat is lost by radiation out into the surroundings and the measured values are therefore less accurate. You can keep the difference sufficiently low by not using too large pieces or volumes of the fuel.
When solid fuels bum in a stream of oxygen, the burning fuel usually emits a blinding light. We therefore recommend that you wear dark-coloured protective glasses, or at least a pair of sunglasses, so that you can read the temperature on the thermometers when combustion. has finished.
The heating values of solid fuels are given in $\mathrm{kJ} / \mathrm{kg}$, those for gaseous fuels predominately in $\mathrm{kJ} / \mathrm{m}^{3}$ but those for liquefied gases also in $\mathrm{kJ} / \mathrm{kg}$.

