

MODULE TITLE : HEAT TRANSFER AND COMBUSTION

TOPIC TITLE : COMBUSTION PROCESSES

**LESSON 2 : HEATING VALUES AND THEIR USE
IN COMBUSTION PROCESSES**

HTC - 4 - 2

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INTRODUCTION

The combustion of fuels is mainly carried out to produce energy for use in chemical processes either directly or via the production of steam.

Each fuel has an enthalpy change when it is burnt in air and values of this change are often given in standard reference books. We will calculate, using these values and a table of enthalpy values for combustion products at various temperatures, the temperature obtainable within the combustion flame (theoretical flame temperature) when the fuel is burnt.

We will also look at furnace efficiency and illustrative temperature – enthalpy ($T - H$) diagrams.

YOUR AIMS

At the end of this lesson you should be able to:

- explain the difference between gross calorific value (higher heating value) and net calorific value (lower heating value)
- understand the term 'heat (enthalpy) of combustion'
- use calorific values/heats of combustion to determine the heat released by single fuels and fuel mixtures
- use temperature – enthalpy tables and/or graphs to obtain enthalpy values for the main products of combustion

- use heat and mass balance to determine
 - flue gas composition
 - theoretical flame temperatures
- produce illustrative temperature-enthalpy diagrams for combustion processes.

STUDY ADVICE

As with the last lesson, you should have already studied similar material when doing the Mass and Energy Balance module. If you have, then this lesson will act as a form of revision. It will not be covered in the detail that it was in Mass and Energy Balance and you may wish to refer to material in that unit if you do not fully understand this lesson.

If you have not studied the Mass and Energy Balance, the work is explained in sufficient detail to answer the questions that will be asked in the Tutor Marked Assignment.

The terms enthalpy and heat are used interchangeably in this lesson, the old term being heat and the new term being enthalpy. However, most text books still refer to heat and hence its use in this lesson.

You will need a calculator and some graph paper when answering some of the questions.

CALORIFIC VALUES

The calorific value (CV) or heating value of a fuel is a measure of the heat evolved when unit mass (1 kg in SI units) or volume (1 m³ in SI units) of a fuel is completely burned. Volume units are used for gases but, in these cases, the conditions of temperature and pressure must be defined and values are quoted generally at a temperature of 15°C (288 K) and a pressure of 1 bar (100 kPa). Note that the standard temperature used for calculating calorific values is 15°C (288 K) when normally temperatures of either 25°C or 0°C are used for other properties.

When obtaining calorific values experimentally, the combustion products are cooled to 15°C (288 K) and heat release includes the latent heat (enthalpy) of vaporisation of water (if present) as the water vapour produced will be condensed to liquid. The CV value obtained in this situation is known as the **gross calorific value (higher heating value)**.

In practice, products of combustion in most processes leave at higher temperatures than 15°C and any water vapour remains in the vapour state. Thus the latent heat of vaporisation is not recovered. The heat released is lower and we have a **net calorific value (lower heating value)**. The net calorific value has to be determined from knowledge of gross calorific value, the fuel analysis and the equations for combustion. It does, however, more accurately represent the actual heat available from the combustion process.

This lower value only applies for fuels that produce water as a product of combustion, i.e. those that contain hydrogen.

Often industrial fuels are mixtures of different compounds and elements, and so calorific value data is normally determined on a complete fuel basis rather than on the individual constituents. However, many gases are obtainable pure,

or nearly pure, and TABLE 1 gives a list of the gross calorific values of some pure gases at a temperature of 15°C and pressure of 1 bar.

<i>Gas</i>	<i>Gross CV MJ m⁻³</i>
<i>Carbon monoxide</i>	<i>11.85</i>
<i>Hydrogen</i>	<i>11.92</i>
<i>Methane</i>	<i>37.07</i>
<i>Ethane</i>	<i>64.46</i>
<i>Propane</i>	<i>93.89</i>
<i>Butane</i>	<i>121.84</i>
<i>Ethylene (ethene)</i>	<i>58.12</i>
<i>Propylene (propene)</i>	<i>85.70</i>

TABLE 1

You may notice that for gases there is an increase in calorific value per m³ with complexity of the molecule. Hydrocarbons burn to produce carbon dioxide, water and heat: the more carbon and hydrogen in the molecule the more heat there is to release. That is, since 1 mole of any gas occupies the same volume at the same conditions of temperature and pressure, a complex gaseous molecule will occupy the same volume as a simple molecule but contain more combustible material.

For information only, approximate gross calorific values of some liquid and solid fuels are listed in TABLE 2. Note that these are per kilogram (kg⁻¹) not per m³.

<i>Liquid fuels</i>	<i>MJ kg⁻¹ (water free)</i>
<i>Kerosene</i>	<i>46.5</i>
<i>Diesel</i>	<i>45.6</i>
<i>Light fuel oil</i>	<i>43.5</i>
<i>Medium fuel oil</i>	<i>43.1</i>
<i>Heavy fuel oil</i>	<i>42.6</i>
<i>Solid fuels (dry, ash-free)</i>	<i>MJ kg⁻¹</i>
<i>Lignite</i>	<i>26.7</i>
<i>High volatile coal</i>	<i>33.7</i>
<i>Low volatile coal</i>	<i>36.5</i>
<i>Athracite</i>	<i>36.3</i>
<i>Wood</i>	<i>19.8</i>

TABLE 2

Calorific values of gaseous fuel mixtures may be estimated by multiplying the volume fraction of each component by its own CV, then summing the results.

We shall calculate the gross CV of the following gas whose composition by volume is:

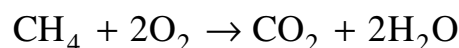
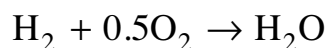
hydrogen (H₂) 50%, carbon monoxide (CO) 45%, methane (CH₄) 5%

Using 1 m³ of gas as a basis, the fuel contains 0.5 m³ of H₂, 0.45 m³ of CO and 0.05 m³ of CH₄. Using these volumes and the figures for CV from TABLE 1,

$$\begin{aligned}
 \text{Gross CV} &= 50\% \text{ of CV for H}_2 + 45\% \text{ of CV for CO} + 5\% \text{ of CV for CH}_4 \\
 &= (0.5 \times 11.92) + (0.45 \times 11.85) + (0.05 \times 37.07) \\
 &= 5.96 + 5.33 + 1.85 \\
 &= 13.14 \text{ MJ m}^{-3}
 \end{aligned}$$

To find the net CV of the same gas, we need to consider the individual reactions and find the water vapour produced by the fuel when it is burnt. Specific heat capacity and latent heat data will then enable us to calculate the heat released when the water vapour produced is cooled and condensed. Let's do this.

For our example fuel, the three reaction equations are



From these equations we can see that 1 mole of H₂ produces 1 mole of H₂O and 1 mole of CH₄ produces 2 moles of H₂O. (Note the carbon monoxide can be ignored as it produces no water.) Since, for gases at the same temperature and pressure, volume % and mol % are interchangeable numerically, we can say that 1 m³ of H₂ will produce 1 m³ of water vapour and 1 m³ of CH₄ will produce 2 m³ of water vapour. For 1 m³ of this fuel, the volume of water vapour produced is equal to the volume of H₂ (0.5 m³) plus twice the volume of CH₄ (0.05 m³), i.e. $0.5 + 2 \times 0.05 = 0.6 \text{ m}^3$. This would be the volume of water vapour produced at 15°C (288 K). We need to convert this volume first to kmoles and then to kg. We do this by using the ideal gas equation.

$$n = \frac{pV}{RT}$$

where n = number of moles
 p = pressure in Pa (1 bar = 100 000 Pa)
 V = volume (m^3)
 R = universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
 T = temperature in kelvin

$$n = \frac{100\,000 \times 0.6}{8.314 \times 288} = 25.1 \text{ mol} = 0.0251 \text{ kmol}$$

Most data for specific heat capacities and specific latent heats are given per kilogram, so we now need to change kmol into kg ($\text{kg} = \text{kmoles} \times \text{molecular mass}$), i.e. $0.0251 \times 18 = 0.452 \text{ kg}$ of water are produced.

The mean specific heat capacity of water from 100°C to $15^\circ\text{C} = 4.20 \text{ kJ kg}^{-1} \text{ K}^{-1}$ and the latent heat of vaporisation of water at 100°C and 1 bar = $2258 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (obtained from steam tables).

Therefore the heat released during the condensation of water vapour and the cooling of the condensate to 15°C

$$\begin{aligned} &= (\text{mass} \times \text{latent heat}) \\ &\quad + (\text{mass} \times \text{specific heat capacity} \times \text{fall in temperature}) \\ &= (0.452 \times 2258) + (0.452 \times 4.20 \times 85) \\ &= 1182 \text{ kJ} \\ &= 1.18 \text{ MJ} \end{aligned}$$

We should, however, take into account that the calorific value would include the gaseous water heat content and we should deduct that from this value. The specific heat capacity of water vapour has a mean value of approximately $1.88 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (from steam tables) and hence the heat in water vapour $= 0.452 \times 1.88 \times 85 = 72 \text{ kJ}$.

Thus total difference $= 1182 - 72 = 1110 \text{ kJ} = 1.11 \text{ MJ}$.

The net CV of the fuel is therefore $= 13.14 - 1.11 = 12.03 \text{ MJ m}^{-3}$.

The value of 1.11 MJ for the difference in heat content between water vapour at 15°C and water at 15°C was for 0.452 kg of water. Thus for 1 kg water, the difference would be $1.11 \div 0.452 = 2.46 \text{ MJ kg}^{-1}$. [This value could have been estimated directly from steam tables by looking at the value of the difference between h_g and h_f for saturated steam at 15°C , i.e. latent heat of water (h_{fg}) at $15^\circ\text{C} = 2.465 \text{ MJ}$.] So for every kilogram of water formed in the combustion of a fuel, the net value of the CV will reduce by 2.46 MJ. Since 1 kilomole of water is 18 kg, the molar value of the heat given out will reduce by $2.46 \times 18 = 44 \text{ MJ kmol}^{-1}$ ($\equiv 44 \text{ kJ mol}^{-1}$).

An alternative to using calorific values, for heat released from a fuel, is to use heat (enthalpy) of combustion (ΔH_{298}°) data. This data is available in textbooks for most single fuels (e.g. in Perry's Chemical Engineer's Handbook there are 3 pages of values for many common hydrocarbon fuels). Some example heats of combustion are given in TABLE 3. The values given are negative values by convention as they are the heat lost by the fuel to its surroundings when it burns. These figures are quoted at a temperature of 25°C and 1 atmosphere pressure and are per mole of the fuel. As with calorific value, they have a lower and higher value depending on whether any water formed is in the liquid (higher) or gaseous (lower) state. They may also have different values based on the state of the fuel before combustion (see butane in the table which has a boiling point of -0.5°C and is often stored as a liquid).

<i>Material</i>	<i>Lower value (kJ mol⁻¹)</i>	<i>Higher value (kJ mol⁻¹)</i>
<i>Hydrogen (H_{2(g)})</i>	-242	-286
<i>Methane (CH_{4(g)})</i>	-803	-891
<i>Propane (C₃H_{8(g)})</i>	-2046	-2222
<i>Liquid butane (C₄H_{10(l)})</i>	-2639	-2859
<i>Gaseous butane (C₄H_{10(g)})</i>	-2660	-2880
<i>Carbon (C_(s))</i>	-394	-394
<i>Carbon monoxide (CO_(g))</i>	-283	-283

TABLE 3

From this table you may be able to see that for each mole of water product formed (or for each mole of H₂ present in the material) the heat of reaction is reduced by 44 kJ (i.e. H₂ has a 44 kJ difference, CH₄ has an 88 kJ difference, C₃H₈ has a 176 kJ difference, etc.). This is the value obtained earlier during our CV calculations.

Also, note that the carbon and carbon monoxide have no difference in higher and lower value as no water is formed in their combustion.

We will now use some of this information and perform a heat balance to determine the **maximum theoretical flame temperature (T_F)** reached when a fuel is burnt. This occurs when the temperature of products is such that

$$\text{heat input to process} = \text{heat out of process}$$

We choose a datum temperature which could be any. In practice, it is often 25°C as combustion data and enthalpy data sources are usually given at this datum (sometimes the datum in some textbooks is 15°C, e.g. when dealing with calorific values).

Heat input = sensible heat in fuel and air
 + heat released by combustion
 (relative to datum temperature)

$$\begin{aligned} \text{Heat out of process} &= \sum (\text{mass} \times \text{mean specific heat capacity} \times T_F) \\ &\quad \text{for each product of combustion} \\ &= \sum (\text{enthalpies of each product of combustion}) \\ &\quad \text{(relative to datum temperature)} \end{aligned}$$

For heat out, one of the values in the equation is itself dependent on temperature (mean specific heat capacity) which, of course, is unknown. To solve the problem, we must first approximate to a solution, do the calculation, refine the estimate, and repeat until we obtain a balance. Fortunately, heat content (enthalpy) data [which is mean specific heat capacity over the range from 25°C to the actual temperature multiplied by the actual temperature] is available – see Appendix – for the products of combustion at various temperatures, and we will make use of these values and a graph to obtain a reasonably accurate solution to the problem of finding the balance temperature. Hopefully this will become clearer as we do a calculation.

Sometimes, the data is a table of mean molar specific heat capacities ($C_{p \text{ mean}}$) for each product of combustion over the range of temperatures given. To calculate enthalpy in this case you multiply the $C_{p \text{ mean}}$ for the temperature by the temperature. We have been kind by doing this for you!! Also, be careful with all data that the units are the correct ones for the calculation – sometimes enthalpies are given in kilocalories!!

Before we use the data in a calculation of flame temperature, we will need to make some assumptions.

- Above 1650°C, errors can arise due to dissociation of water vapour and carbon dioxide, giving lower flame temperatures, but we will not get involved with that difficulty here.
- The process is adiabatic (no external heat is added to, or removed from, the process).
- All the fuel is burnt (though in some calculations, combustion may not be completely to carbon dioxide and water and some carbon monoxide may be formed).
- Fuel and air enter at datum conditions – usually 25°C (though the calculation can be adjusted to any temperature).
- Combustion products emerge at a single temperature.

To calculate the flame temperature, we will first find the heat present in, and generated by, the fuel and air (heat in), then we will need to calculate the amounts and composition of the product gases. We can then find the enthalpy figures (heat out) for each product gas at 'selected' temperatures and thus the total heat out by estimation of a flame temperature. Finally, we need to refine and repeat our calculations until we find the 'actual' temperature where the heat in = heat out, i.e. they balance and this is the maximum theoretical flame temperature for the supply conditions of fuel and air.

Let's do an example of a flame temperature calculation utilising this series of steps to help show this process.

Example 1

A fuel gas has the composition 90% CH₄ (methane), 10% C₃H₈ (propane) by volume. It is completely combusted with 30% excess air at a temperature of 25°C. The heats of combustion are

$$\Delta H_{298}^{\circ} \text{CH}_4 = -803 \text{ kJ mol}^{-1}, \quad \Delta H_{298}^{\circ} \text{C}_3\text{H}_8 = -2045 \text{ kJ mol}^{-1}$$

Calculate the theoretical flame temperature reached.

The values for ΔH_{298}° are the lower values given in TABLE 3. Why?

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These are the lower values as we will have a flame temperature well above the condensing point of water and thus we will not get the benefit of the latent heat of vaporisation of water.

Solution

We will assume the datum temperature of 25°C which is very convenient as the temperature of fuel and air into the process is 25°C, the heat of combustion for each fuel is at 25°C and the enthalpy data given in the Appendix has a datum of 25°C!

If the fuel and air were at a higher (or lower) temperature we would have to calculate their additional (reduced) heat content relative to 25°C using:

$$\begin{aligned} \text{Additional (reduced) heat content} \\ = \text{mass} \times \text{specific heat capacity} \times \text{temperature difference} \end{aligned}$$

This would be, in effect, additional (reduced) heat supplied to the combustion process, i.e. additional (reduced) heat input.

As the fuel and air in this question are at 25°C (our datum), the only heat input is from the heat of combustion of each fuel.

Let's start with the assumption that we have **1 mole of fuel** (we could choose any amount but by choosing 1 mole we make the calculations easier as most of the figures quoted in the question are per mole). As the composition of the fuel is given in volume %, which is the same as mole % for gaseous fuels, we can convert the volume into moles to give us a fuel composition of 0.9 mol CH₄ and 0.1 mol C₃H₈.

Thus, heat released by combustion of 1 mole of the fuel

$$\begin{aligned} &= 0.9 \times \Delta H_{298}^{\circ} \text{CH}_4 + 0.1 \times \Delta H_{298}^{\circ} \text{C}_3\text{H}_8 \\ &= 0.9 \times 803 + 0.1 \times 2045 \\ &= 927.2 \text{ kJ} \end{aligned}$$

(We have ignored the negative sign associated with the heat of combustion as we know the heat is given out by the fuel and therefore is a heat input to the process.)

So, the total heat in = $927.2 \text{ kJ (mol fuel)}^{-1}$.

To find the heat out, we now need to find the amount and composition of the flue gas produced when 1 mole of the fuel is completely combusted. To do this we need to write the balanced equations for the combustion of each fuel and then use these to determine the theoretical and actual amounts of O_2 and N_2 supplied, and CO_2 and H_2O formed, for combustion of 1 mole of fuel (0.9 mol CH_4 and 0.1 mol C_3H_8).

Can you produce balanced equations for the complete combustion of CH_4 and C_3H_8 ? Remember the products are always carbon dioxide (CO_2) and water (H_2O).

The answers are in the text that follows.

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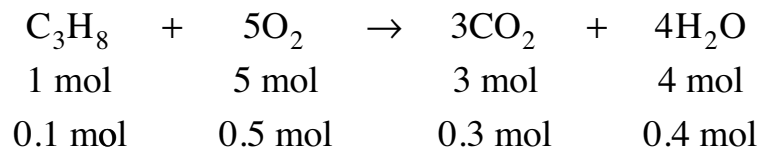
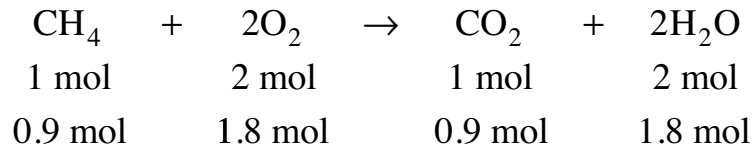
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The balanced combustion equations and amounts of products formed from our fuel mixture are



From this we can see that, in theory, to burn 1 mole of fuel mix we require 2.3 (1.8 + 0.5) mol O₂, and 1.2 (0.9 + 0.3) mol of CO₂ and 2.2 (1.8 + 0.4) mol of H₂O are produced in the flue gas.

The question states that we have 30% excess air (oxygen), so the actual amount of oxygen supplied = theoretical × 1.3 = 2.3 × 1.3 = 2.99 mol of which 2.3 mol are used for combustion and 0.69 mol will be present in the flue gas.

Nitrogen (N₂) associated with the oxygen supply

$$= 2.99 \times 3.76$$

(where 3.76 is the conversion factor from oxygen
in air to nitrogen [79% ÷ 21%])

$$= 11.24 \text{ moles}$$

All this N₂ passes through the combustion process unchanged so appears in the flue gas.

The flue gas therefore contains

H ₂ O	–	2.2 moles
CO ₂	–	1.2 moles
O ₂	–	0.69 moles
N ₂	–	11.24 moles

giving a total of 15.33 moles

Summarising the results in a table (TABLE 4):

<i>Feed</i>		<i>O₂ used</i>	<i>Flue gases</i>			
<i>Material</i>	<i>moles</i>		<i>CO₂ produced</i>	<i>H₂O produced</i>	<i>N₂</i>	<i>O₂</i>
<i>Methane CH₄</i>	<i>0.9</i>	<i>1.8</i>	<i>0.9</i>	<i>1.8</i>	–	–
<i>Propane C₃H₈</i>	<i>0.1</i>	<i>0.5</i>	<i>0.3</i>	<i>0.4</i>		
<i>Oxygen O₂</i>	<i>2.99</i>	<i>–2.99</i>				<i>0.69</i>
<i>Nitrogen N₂</i>	<i>11.24</i>	<i>0</i>			<i>11.24</i>	
<i>Total</i>	<i>15.33</i>	<i>–0.69</i>	<i>1.2</i>	<i>2.2</i>	<i>11.24</i>	<i>0.69</i>

TABLE 4

Knowing the amount of each combustion gas we can determine their heat content if we know their mean molar heat capacity and their temperature (enthalpy mol⁻¹). We now need to look at the table in the Appendix which shows the enthalpy mol⁻¹ of the various combustion gases at different temperatures. We will be mainly concentrating on the range 1500 – 2100°C as this is the expected range of flame temperatures. [Note: the values are given in the table as MJ kmol⁻¹ which is the same numerically as kJ mol⁻¹.]

Let's assume a flame temperature of 2000°C and, using the values in the table (highlighted in TABLE 5), we will calculate the heat content of each component of flue gas and thus the total heat content of the flue gas.

<i>Temperature °C</i>	<i>Enthalpy (MJ kmol⁻¹ or kJ mol⁻¹)</i>					
	<i>H₂</i>	<i>N₂</i>	<i>CO</i>	<i>CO₂</i>	<i>O₂</i>	<i>H₂O</i>
2000	62.41	66.10	66.72	108.32	69.65	86.24

TABLE 5

Heat content = enthalpy (kJ mol⁻¹) × no. of moles

For N₂, heat content = 66.10 × 11.24 = 742.96 kJ

For CO₂, heat content = 108.32 × 1.2 = 129.98 kJ

For O₂, heat content = 69.65 × 0.69 = 48.06 kJ

For H₂O, heat content = 86.24 × 2.2 = 189.73 kJ

Total = 1110.73 kJ

This is much more than the heat available from the combustion (927.2 kJ). So the estimated temperature is too high.

Let us repeat for a lower temperature of 1800°C (see TABLE 6 for values)

<i>Temperature °C</i>	<i>Enthalpy (MJ kmol⁻¹)</i>					
	<i>H₂</i>	<i>N₂</i>	<i>CO</i>	<i>CO₂</i>	<i>O₂</i>	<i>H₂O</i>
1800	55.49	58.89	59.46	96.16	62.05	76.10
1900	58.92	62.46	63.06	102.13	65.81	81.17

TABLE 6

For N_2 , heat content = $58.89 \times 11.24 = 661.92 \text{ kJ}$

For CO_2 , heat content = $96.16 \times 1.2 = 115.39 \text{ kJ}$

For O_2 , heat content = $62.05 \times 0.69 = 42.81 \text{ kJ}$

For H_2O , heat content = $76.10 \times 2.2 = 167.42 \text{ kJ}$

Total = 987.54 kJ

This is still more than the heat available from the combustion (927.2 kJ). So this estimated temperature is too high. The answer should be below 1800°C.

You try repeating the calculation for a temperature of 1700°C. The information is given in the Appendix.

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From the Appendix:

$$\text{For N}_2, \text{ heat content} = 55.25 \times 11.24 = 621.01 \text{ kJ}$$

$$\text{For CO}_2, \text{ heat content} = 89.06 \times 1.2 = 106.87 \text{ kJ}$$

$$\text{For O}_2, \text{ heat content} = 58.24 \times 0.69 = 40.19 \text{ kJ}$$

$$\text{For H}_2\text{O, heat content} = 71.04 \times 2.2 = 156.29 \text{ kJ}$$

$$\text{Total} = 924.36 \text{ kJ}$$

This is now less than the heat available from the combustion (927.2 kJ). So this temperature is too low. The temperature is therefore between 1700 and 1800°C.

What do we do now? We do not have any further data for temperatures between 1700 and 1800°C to use in our calculations.

The simplest solution is to assume that there is a straight line relationship between the enthalpies of the gases at 1700 and 1800°C. We can draw a graph of enthalpy against temperature between 1700°C (enthalpy = 924.36) and 1800°C (enthalpy = 987.54) and interpolate the temperature when the enthalpy is 927.2 kJ as shown in FIGURE 1.

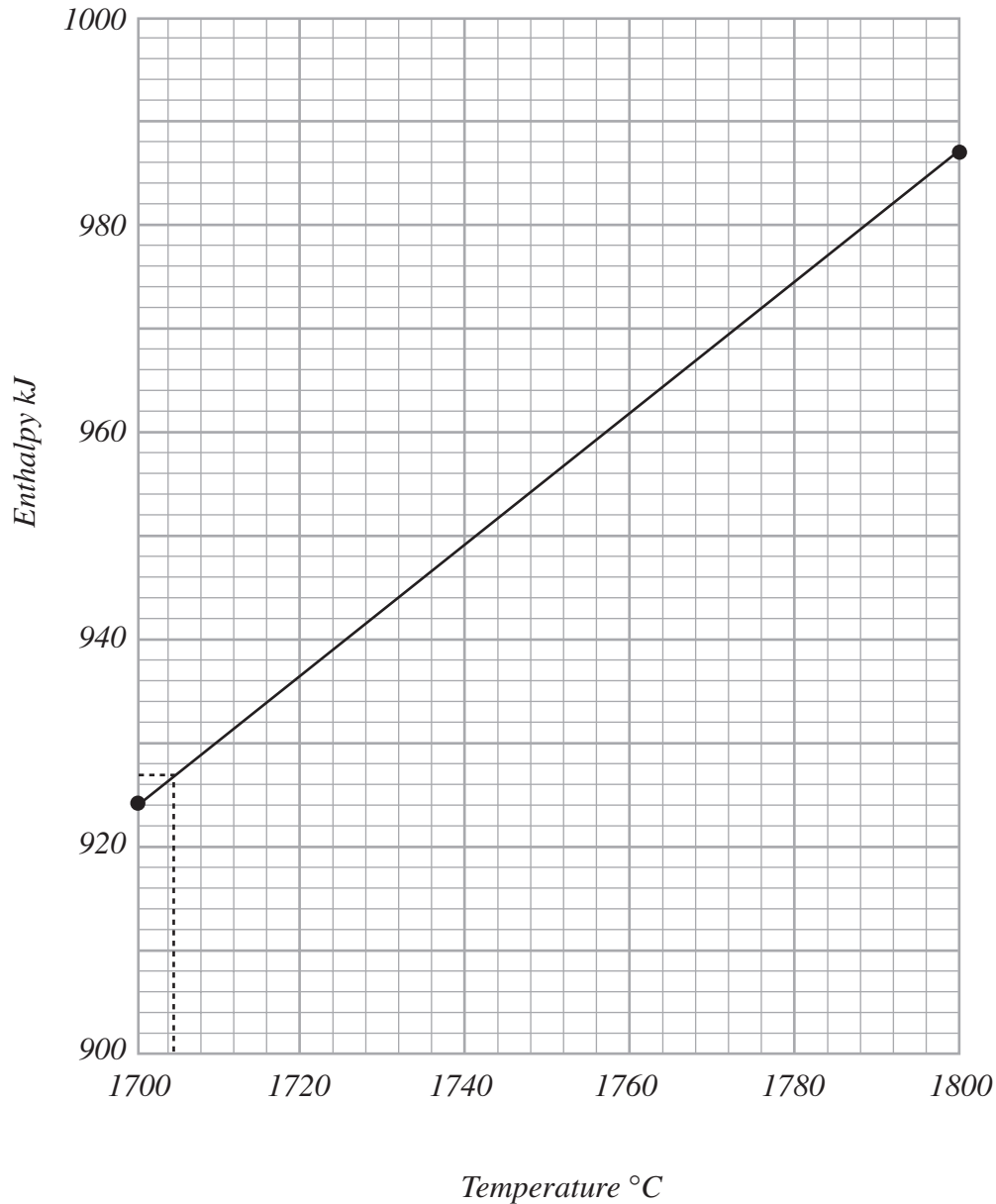


FIG. 1

This gives a flame temperature of 1705°C.

The actual graph would be slightly curved in practice. The error created by using a straight line is small but if a more accurate result is required there are spreadsheets which will enable calculations to be done more accurately. However, this answer is sufficiently accurate for our (and most) purposes!

Solving this problem has been a rather long process with lots of repetitive calculations. In industry there are computer programs which will perform the calculations to a high degree of accuracy, but it is important you are aware of the method so that you can quickly check to see that the programs are performing correctly and giving the right order of result.

This question was a relatively straightforward one to solve. Let's look at another problem which adds a few complications.

Example 2

A fuel gas has a net calorific value of 52.5 MJ m^{-3} when it is measured at 15°C and 1.013 bar pressure. It is burnt with 70% excess air, both fuel and air at a temperature of 260°C , to give a wet flue gas analysis of

$$\text{CO}_2 \text{ 6\%, } \text{H}_2\text{O 11.4\%, } \text{O}_2 \text{ 8.1\%, } \text{N}_2 \text{ 74.5\%}$$

The theoretical air supply is known to be 10.24 kmol per kmol of fuel.

The mean molar heat capacity of the fuel/air mix is $30 \text{ kJ kmol}^{-1} \text{ K}^{-1}$ (for a temperature range of $15 - 300^\circ\text{C}$).

Calculate the flame temperature.

Solution

The datum temperature we will use will once again be 25°C. This does create a slight error in that the CV is quoted at 15°C and we should really do a recalculation of the CV involving the difference in specific heat capacities between products and reactants for a temperature difference of 10°C (from 15 to 25°C). However, we are not given values for specific heat capacities for the products of combustion between 15 and 25°C (though we could estimate them from the table in the Appendix or look them up in reference books). Since the reactants and products are predominately nitrogen from the air and the temperature difference is relatively small, we will assume this difference in specific heat capacities between reactants and products will be negligible.

Before we can really start, we need to convert the CV to units of kmol^{-1} instead of m^{-3} so we can make the units consistent throughout the calculation.

What is the link between volume occupied and moles present for gases?

.....

You should remember that 1 kmol of any gas occupies 22.4 m^3 at 0°C and 1.013 bar (1 atmosphere). Alternatively we can use the ideal gas equation $pV = nRT$ where n = number of moles, R = universal gas constant and T = temperature (K).

To make use of the first method, we need to convert the volume of 1 m^3 of fuel at 15°C (288 K) to a volume at 0°C (273 K) using Charles' law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

where V = volume and T = temperature in kelvin.

Thus new volume $V_2 = \frac{V_1 T_2}{T_1} = \frac{1 \times 273}{288} = 0.948 \text{ m}^3$ at 0°C

$$\text{Now converting to kmol} = \frac{\text{actual volume at } 0^\circ\text{C}}{\text{volume of 1 kmol at } 0^\circ\text{C}}$$

Number of kmol fuel in 0.948 m^3 of gas at 0°C (\equiv number of kmol fuel in 1 m^3 at 15°C)

$$= \frac{0.948}{22.4} = 0.0423 \text{ kmol}$$

[Alternatively, using $pV = nRT$ for $p = 1.013 \text{ bar} = 101\,300 \text{ Pa}$, $V = 1 \text{ m}^3$, $T = 288 \text{ K}$ and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$n = \frac{pV}{RT} = \frac{101\,300 \times 1}{8.314 \times 288} = 42.3 \text{ mol} = 0.0423 \text{ kmol}]$$

Thus the CV of the fuel = $\frac{\text{CV in MJ m}^{-3} (\text{at } 15^\circ\text{C})}{\text{number of kmol m}^{-3} (\text{at } 15^\circ\text{C})}$

$$= \frac{52.5}{0.0423} = 1241.1 \text{ MJ kmol}^{-1} \text{ at } 15^\circ\text{C}$$

For 1 kmol fuel completely combusted at 15°C, the heat released is therefore 1241.1 MJ. We will assume, as stated earlier, that this molar value has the same value at 25°C.

We now need to calculate the heat available as preheat in the air/fuel mix at 260°C relative to 25°C.

The question tells us the theoretical air:fuel ratio is 10.24 kmol air (kmol fuel)⁻¹ and we have a 70% excess of air for this reaction.

Thus the actual amount of air supplied = $10.24 \times 1.7 = 17.41$ kmol of which 79% is nitrogen (N₂) = $0.79 \times 17.41 = 13.75$ kmol and 21% is oxygen (O₂) = $0.21 \times 17.41 = 3.66$ kmol.

(1.7 = conversion factor from theoretical air supply to actual for a 70% excess.)

The air/fuel mix therefore has a total of 17.41 kmol air + 1 kmol fuel = 18.41 kmol mix.

The mean molar heat capacity of the air:fuel mix is given as 30 kJ kmol⁻¹ K⁻¹ and thus its heat content relative to 25°C is

$$= \text{mass (mol)} \times \text{mean molar heat capacity} \\ \times \text{temperature difference (in } ^\circ\text{C or K)}$$

$$= 18.41 \times 30 \times (260 - 25)$$

$$= 129\,790 \text{ kJ}$$

$$= 129.8 \text{ MJ}$$

So total heat input per kmol of fuel

$$= CV + \text{additional heat content of reactants}$$

$$= 1241.1 + 129.8$$

$$= 1370.9 \text{ MJ}$$

Now we need to know what the flue gas amount and composition are to be able to do the heat balance.

From our earlier calculation, we know that there are 13.75 kmol of N_2 in the air supply and this will pass through unchanged (nitrogen always does). However, the question states that the N_2 in the flue gas is 74.5% of the total flue gas (wet).

Thus if 13.75 kmol is 74.5% of flue gas, 100% of flue gas $= \frac{13.75}{74.5} \times 100$
 $= 18.46$ kmol.

From this overall figure, we can calculate the amount of each component in the flue gas since we are given the % of each component.

$$CO_2 = 6\% \text{ of total} = 0.06 \times 18.46 = 1.11 \text{ kmol}$$

$$H_2O = 11.4\% \text{ of total} = 0.114 \times 18.46 = 2.10 \text{ kmol}$$

$$O_2 = 8.1\% \text{ of total} = 0.081 \times 18.46 = 1.50 \text{ kmol}$$

$$N_2 = 74.5\% \text{ of total} = 0.745 \times 18.46 = 13.75 \text{ kmol}$$

The problem now becomes the same as in the previous example, to find the temperature where heat in = heat out in flue gas.

As the fuel and air were preheated in this example, we can assume the temperature this time will be higher than the previous one of 1705°C.

Let's go for 2000°C as a start. Using the information highlighted in TABLE 7:

<i>Temperature °C</i>	<i>Enthalpy (MJ kmol⁻¹)</i>					
	<i>H₂</i>	<i>N₂</i>	<i>CO</i>	<i>CO₂</i>	<i>O₂</i>	<i>H₂O</i>
2000	62.41	66.10	66.72	108.32	69.65	86.24
2100	65.92	69.74	70.38	114.42	73.50	91.39

TABLE 7

$$\text{Heat content} = \text{enthalpy mol}^{-1} \times \text{no. of moles}$$

$$\text{For N}_2, \text{ heat content} = 66.10 \times 13.75 = 908.9 \text{ MJ}$$

$$\text{For CO}_2, \text{ heat content} = 108.32 \times 1.11 = 120.2 \text{ MJ}$$

$$\text{For O}_2, \text{ heat content} = 69.65 \times 1.5 = 104.5 \text{ MJ}$$

$$\text{For H}_2\text{O}, \text{ heat content} = 86.24 \times 2.1 = 181.1 \text{ MJ}$$

$$\text{Total} = 1314.7 \text{ MJ}$$

This is still too low as the heat in = 1370.9 MJ

You try 2100°C. Information required is highlighted in TABLE 8.

<i>Temperature °C</i>	<i>Enthalpy (MJ kmol⁻¹)</i>					
	<i>H₂</i>	<i>N₂</i>	<i>CO</i>	<i>CO₂</i>	<i>O₂</i>	<i>H₂O</i>
2100	65.92	69.74	70.38	114.42	73.50	91.39

TABLE 8

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$$\text{For } N_2, \text{ heat content} = 69.74 \times 13.75 = 958.9 \text{ MJ}$$

$$\text{For } CO_2, \text{ heat content} = 114.42 \times 1.11 = 127.0 \text{ MJ}$$

$$\text{For } O_2, \text{ heat content} = 73.50 \times 1.5 = 110.3 \text{ MJ}$$

$$\text{For } H_2O, \text{ heat content} = 91.39 \times 2.1 = 191.9 \text{ MJ}$$

$$\text{Total} = 1388 \text{ MJ}$$

This is higher than the heat input of 1370.9 MJ. We need to do a graph as before and this is shown in FIGURE 2. It gives a flame temperature of 2077°C.

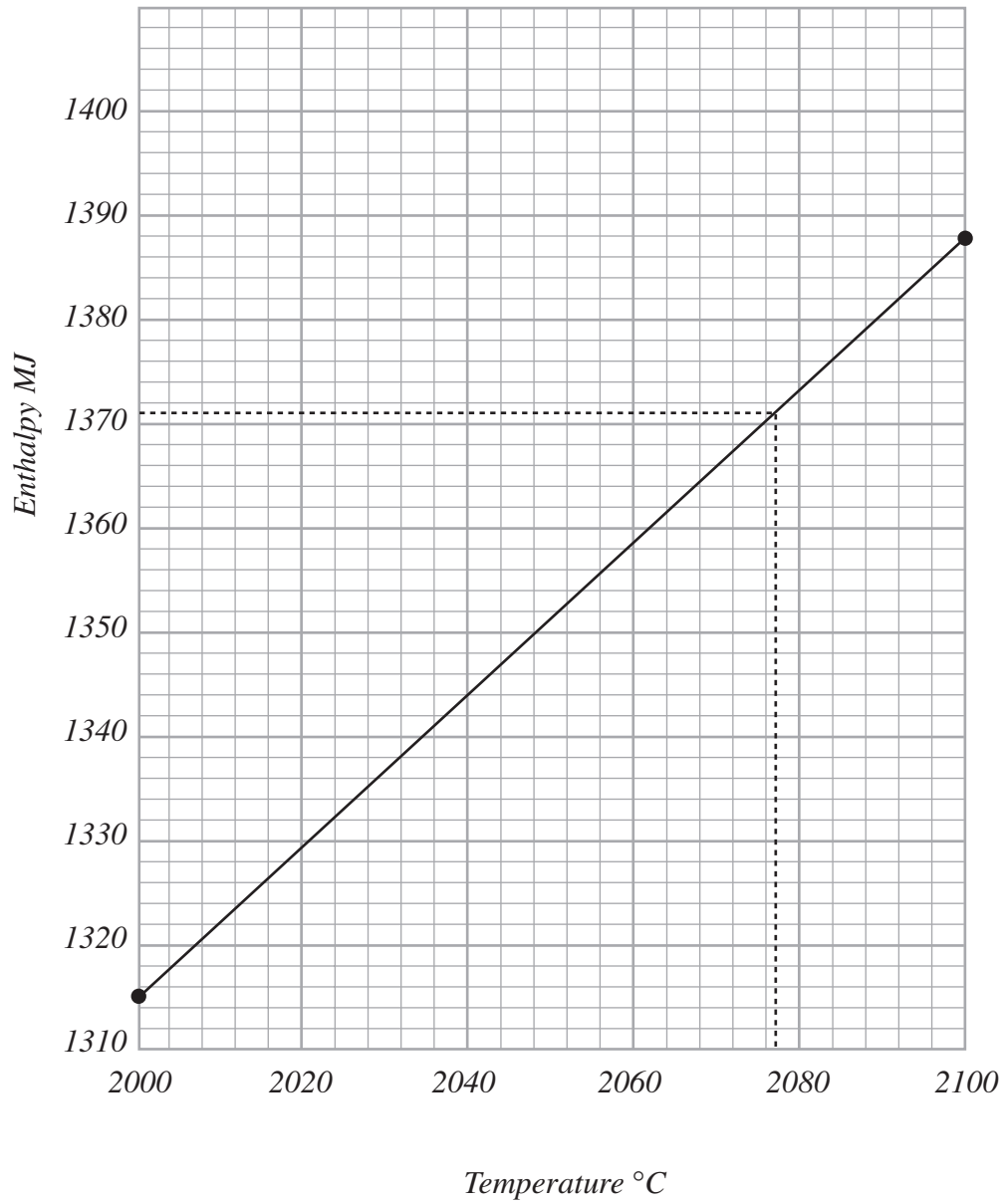


FIG. 2

OVERALL TEMPERATURE – ENTHALPY (T – H) DIAGRAMS

When we consider processes involving heat transfer it is sometimes useful to illustrate the process using what are known as temperature – enthalpy ($T - H$) diagrams. The following will show how the two examples we have just completed are illustrated. Note that these diagrams are **not to scale** and are for illustration purposes only.

The basis of these diagrams is two lines, one representing the change in total enthalpy with temperature of the fuel and air – the reactants line – (note this includes the internal energy stored in the structure of the fuel), and the other shows the change in enthalpy with temperature for the products of combustion (also including energy stored in the structure of each material). The products line is below the level of the reactants line as the products have less internal energy stored in their structure than the reactants. It is the difference in this internal energy between reactants and products that is released by combustion.

The diagram overleaf (FIGURE 3) shows Example 1 where the fuel and air (reactants) were initially at 25°C, with an initial total enthalpy of h_i . As combustion occurs energy is released as heat (the heat of combustion) and this is the source of heat used to heat up the products of combustion. This heat is used to increase the enthalpy of the products until a point is reached where the initial total enthalpy of reactants = final enthalpy of the products (flue gas). At this point, the final temperature (1705°C) is the maximum temperature reached and is the flame temperature. This has assumed no heat is lost from the process or added to the process (an adiabatic process). The progress of the process is highlighted.

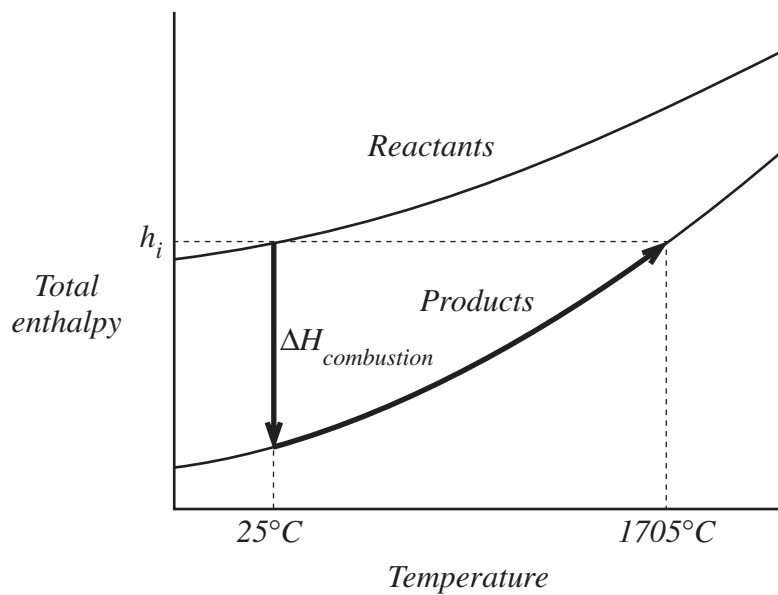


FIG. 3 Example 1

The diagram in FIGURE 4 shows Example 2, where the fuel/air mix is initially at a temperature of 260 °C and thus has additional heat content due to the increase in temperature of reactants above the datum of 25°C. In theory, we could cool the reactants down to 15°C (recovering the heat) then carry out the reaction releasing the CV and then use the heat energy released and recovered to heat up the products to the same total enthalpy as the initial fuel and air at 260°C. This is the process highlight in FIGURE 4.

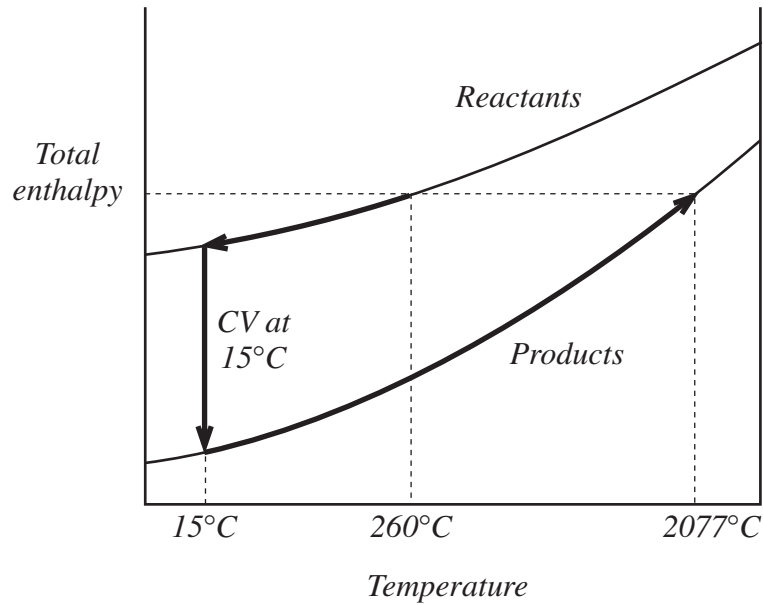


FIG. 4 Example 2

In reality, the process is as shown in FIGURE 5. The air and fuel are preheated (by whatever method) to a higher enthalpy input, combustion then occurs at the higher temperature, and the heat released heats the products to a final temperature where total enthalpy in = total enthalpy out.

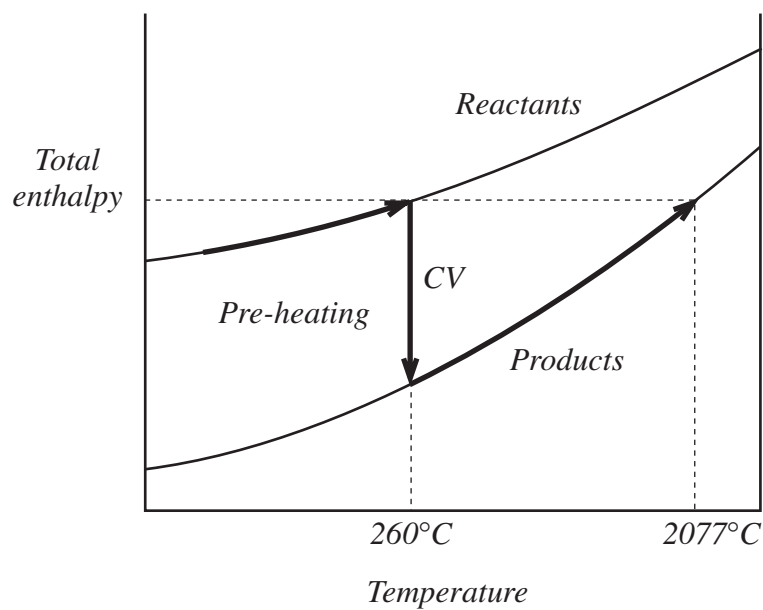


FIG. 5

FURNACE EFFICIENCY

Flame temperature is the temperature of the flame at the point of combustion, i.e. the burner. It is the highest temperature attained in a furnace under theoretical conditions for a given fuel/air combination. Its value is dependent on complete combustion and thus on the amount of excess air. Too much air and the temperature will be lowered due to the excess air taking away heat from the burner. Too little air and the fuel may be starved of oxygen and not be completely burnt to carbon dioxide and water and thus will release less energy (lower heat of combustion). This in turn will reduce the flame temperature. The flame temperature may also be reduced further by any heat losses from the flame to its surroundings (our calculations assumed no heat loss).

For maximum actual flame temperature, therefore, proper monitoring of the condition of combustion equipment and air:fuel flows is essential to minimise poor combustion and heat losses.

The **efficiency of heat transfer from a flame** is given by:

$$\text{furnace efficiency} = \frac{T_2 - T_1}{T_2}$$

where T_2 is the actual flame temperature and T_1 is the outlet temperature of the flue gases in kelvin.

Efficiency can only be improved by either raising the flame temperature or reducing the outlet temperature of the flue gas. The latter is usually fixed by the process using the heat, so maximum efficiency is obtained by maximising flame temperature. As we have already said this is done by minimising the amount of excess air without affecting complete combustion and by minimising heat loss to the surroundings.

You have now completed this lesson and should attempt the Self-Assessment Questions which follow to test your understanding.

SELF-ASSESSMENT QUESTIONS

1. (a) What is the difference between the gross calorific value (higher heating value) and net calorific value (lower heating value) of a fuel?

(b) Which types of fuel will have lower heating values?

2. Using the values given in the lesson, determine the calorific value of a fuel which has the following composition by volume:

60% H₂, 30% CH₄ (methane), 10% C₂H₆ (ethane).

3. Determine the theoretical flame temperature for the following **gaseous** fuel which is burnt with 35% excess air at 25°C.

Fuel composition by volume: propane (C₃H₈) 75%, butane (C₄H₁₀) 25%.

Use values given in the lesson for heats of combustion and enthalpy of combustion products.

Assume a first estimate of 1700°C.

ANSWERS TO SELF-ASSESSMENT QUESTIONS

1. (a) The gross calorific value (higher heating value) is where the water in the combustion products has been condensed and forms a liquid product thus releasing its latent heat of vaporisation. The net calorific value (lower heating value) of a fuel is where the water remains as a vapour and retains its latent heat.
- (b) Only those fuels which produce water as a product will have a lower value.
2. In 1 m³ of fuel at 15°C, based on fuel analysis, there are:

$$0.6 \text{ m}^3 \text{ H}_2$$

$$0.3 \text{ m}^3 \text{ CH}_4$$

$$0.1 \text{ m}^3 \text{ C}_2\text{H}_6$$

The gross CV of each fuel from TABLE 1 is

$$\text{H}_2 = 11.92 \text{ MJ m}^{-3}$$

$$\text{CH}_4 = 37.07 \text{ MJ m}^{-3}$$

$$\text{C}_2\text{H}_6 = 64.46 \text{ MJ m}^{-3}$$

$$\text{CV of fuel} = \sum (\text{volume} \times \text{CV}) \text{ for each component}$$

$$= (0.6 \times 11.92) + (0.3 \times 37.07) + (0.1 \times 64.46)$$

$$= 24.719 \text{ MJ m}^{-3}$$

3. Datum 25°C.

Assume 1 mole of fuel mix which is 75% C₃H₈ and 25% C₄H₁₀. The fuel mix will be made up of 0.75 mol C₃H₈ and 0.25 mol C₄H₁₀.

Need to calculate the heat of combustion of the fuel mix. To do this use the lower values of heat of combustion as water stays as a vapour.

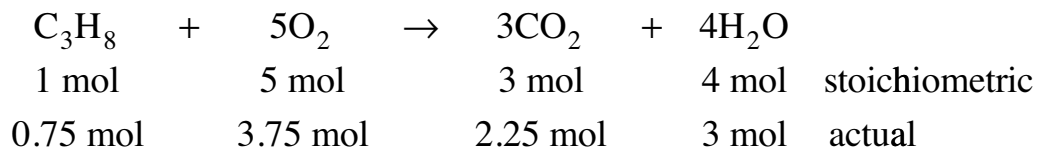
Heat of combustion of fuel mix

$$\begin{aligned}
 &= \text{amount of C}_3\text{H}_8 \times \Delta H_{298, \text{C}_3\text{H}_8}^\circ + \text{amount of C}_4\text{H}_{10} \times \Delta H_{298, \text{C}_4\text{H}_{10}}^\circ \\
 &= 0.75 \times 2046 + 0.25 \times 2660 \\
 &= 2199.5 \text{ kJ mol}^{-1}
 \end{aligned}$$

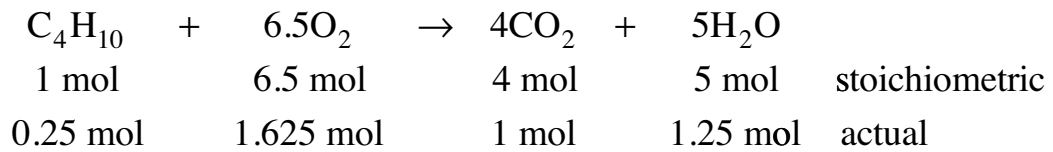
$$\begin{aligned}
 \text{Heat input to process} &= \text{heat of combustion of fuel mix} \\
 &\quad \text{(fuel mix supplied at datum)} \\
 &= 2199.5 \text{ kJ mol}^{-1}
 \end{aligned}$$

Now need the balanced equations to determine amount of air and combustion products first by reaction stoichiometry and then by the actual figures for each fuel. These are given below.

For propane



For butane



Thus, adding the actual values for propane and butane,

Amount of O_2 theoretically required for complete combustion

$$= 3.75 + 1.625$$

$$= 5.375 \text{ mol}$$

With a 35% excess, actual amount supplied

$$= 5.375 \times 1.35$$

$$= 7.256 \text{ mol}$$

of which $7.256 - 5.375 = 1.881 \text{ mol}$ (the excess) will be present in the flue gas.

Nitrogen (N_2) associated with the oxygen supply

$$= 7.256 \times 3.76$$

$$= 27.28 \text{ mol}$$

All of this is present in the flue gas as it passes through unchanged.

$$\text{CO}_2 \text{ formed} = 2.25 + 1 = 3.25 \text{ mol}$$

$$\text{H}_2\text{O formed} = 3 + 1.25 = 4.25 \text{ mol}$$

So the flue gas composition is:

$$\text{O}_2 = 1.881 \text{ mol}$$

$$\text{N}_2 = 27.28 \text{ mol}$$

$$\text{CO}_2 = 3.25 \text{ mol}$$

$$\text{H}_2\text{O} = 4.25 \text{ mol}$$

Now need to calculate the heat content of flue gases at various temperatures. Assuming a temperature of 1700°C and obtaining the enthalpy figures from the Appendix (highlighted in TABLE 9 below):

<i>Temperature °C</i>	<i>Enthalpy (MJ kmol⁻¹)</i>					
	<i>H₂</i>	<i>N₂</i>	<i>CO</i>	<i>CO₂</i>	<i>O₂</i>	<i>H₂O</i>
1600	48.70	51.72	52.24	84.08	54.53	65.61
1700	52.04	55.25	55.81	89.06	58.24	71.04
1800	55.49	58.89	59.46	96.16	62.05	76.10

TABLE 9

$$\text{O}_2 = 1.881 \times 58.24 = 109.5 \text{ kJ}$$

$$\text{N}_2 = 27.28 \times 55.25 = 1507.2 \text{ kJ}$$

$$\text{CO}_2 = 3.25 \times 89.06 = 289.4 \text{ kJ}$$

$$\text{H}_2\text{O} = 4.25 \times 71.04 = 301.9 \text{ kJ}$$

$$\text{Total} = 2208 \text{ kJ}$$

This is higher than heat in value of 2199.5 kJ, so repeat for 1600°C.

Heat content at 1600°C:

$$\text{O}_2 = 1.881 \times 54.53 = 102.6 \text{ kJ}$$

$$\text{N}_2 = 27.28 \times 51.75 = 1411.7 \text{ kJ}$$

$$\text{CO}_2 = 3.25 \times 84.08 = 273.3 \text{ kJ}$$

$$\text{H}_2\text{O} = 4.25 \times 65.61 = 278.8 \text{ kJ}$$

$$\text{Total} = 2066.4 \text{ kJ}$$

This is lower than the heat input value of 2199.5 kJ so flame temperature is between 1600 and 1700°C.

Produce graph (FIGURE 6) to determine flame temperature = 1694°C.

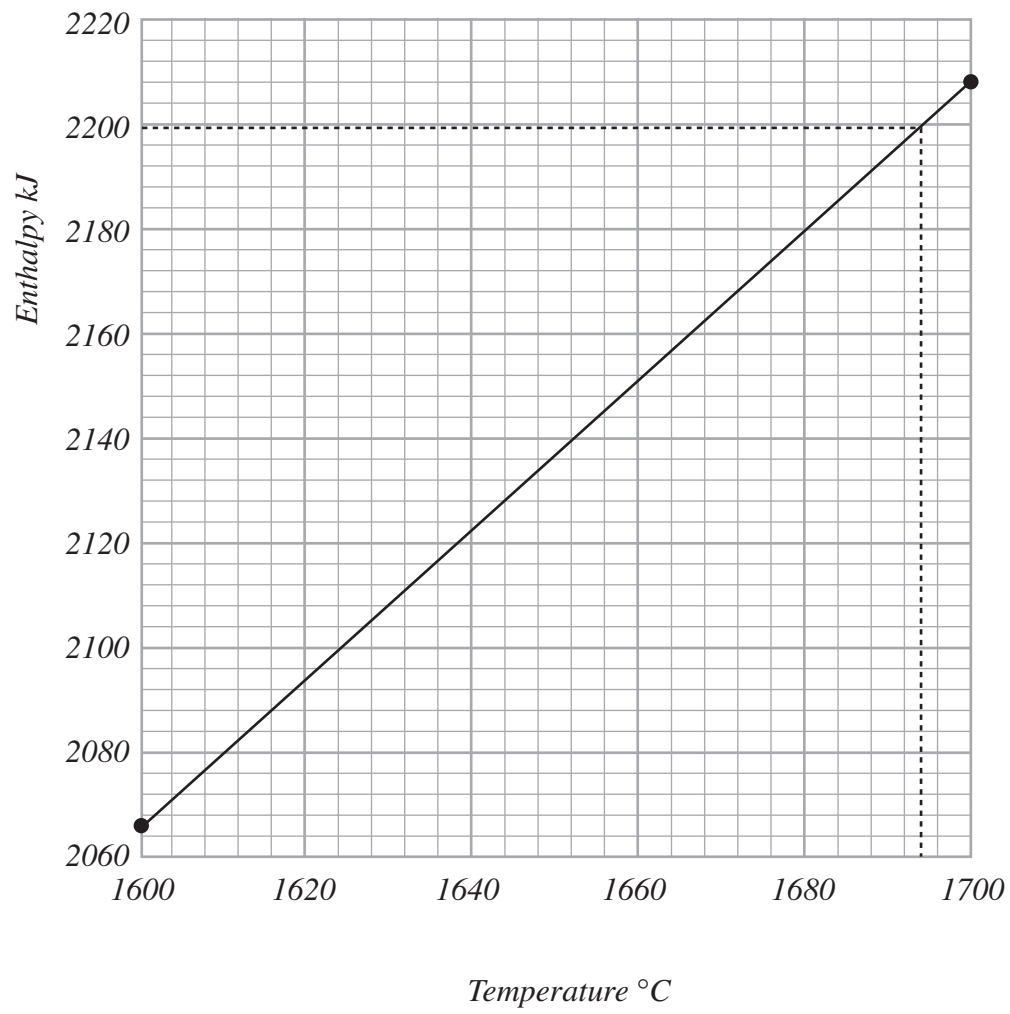


FIG. 6

SUMMARY

In this lesson we have looked at heat released during combustion and the two main ways of expressing this:

- Calorific value – the heat released per m^3 (for gases) or per kg (for solids and liquids) of fuel. These are usually quoted at 15°C . The difference between gross calorific value (higher heating value), which has the water present as liquid and thus includes recovered latent heat of vaporisation, and net calorific value (lower heating value), which has the water present as vapour, was also covered. This difference is approximately 2.46 MJ kg^{-1} or 44 MJ mol^{-1} of water produced in the combustion process.
- Heat (enthalpy) of combustion – the heat released by combustion per mole of material at 25°C . It also has higher and lower values if water is produced by the combustion process.

We then used calorific values/heats of combustion to determine the heat released by single fuels and fuel mixtures and thus the heat input to a process.

Since a heat balance will mean that

$$\text{heat input to a process} = \text{heat output in flue gases}$$

we can use the heat input value and enthalpy tables for the main products of combustion, to obtain this balance and determine the theoretical flame temperature. This involves graphical interpolation of results to get a reasonably accurate estimate.

To achieve this we had to determine the amount and composition of flue gases using material/mass balances from balanced reaction equations and a knowledge of excess air requirements.

A high flame temperature is important to the efficiency of the furnace (the place combustion occurs) and this is maximised by careful monitoring of air/fuel ratio and equipment condition.

We also produced illustrative temperature – enthalpy ($T - H$) diagrams for combustion processes.

APPENDIX

Temperature °C	Enthalpy (MJ kmol ⁻¹)					
	H ₂	N ₂	CO	CO ₂	O ₂	H ₂ O
25	0.00	0.00	0.00	0.00	0.00	0.00
100	2.17	2.19	2.19	2.90	2.22	2.54
200	5.10	5.13	5.14	7.11	5.26	5.99
300	8.03	8.10	8.14	11.64	8.40	9.46
400	10.96	11.13	11.20	16.43	11.63	13.20
500	13.91	14.24	14.34	21.43	14.95	16.98
600	16.88	17.40	17.55	26.61	18.33	20.89
700	19.87	20.62	20.81	31.94	21.78	24.91
800	22.91	23.91	24.15	37.41	25.28	29.08
900	25.92	27.27	27.55	43.01	28.85	33.37
1000	29.10	30.64	30.97	48.66	32.42	37.74
1100	32.27	34.09	34.44	54.46	36.05	42.26
1200	35.46	37.56	37.95	60.26	39.69	46.85
1300	38.71	41.06	41.49	66.14	43.36	51.57
1400	41.96	44.55	45.01	71.96	47.01	56.24
1500	45.24	48.08	48.58	78.37	50.66	61.08
1600	48.70	51.72	52.24	84.08	54.53	65.61
1700	52.04	55.25	55.81	89.06	58.24	71.04
1800	55.49	58.89	59.46	96.16	62.05	76.10
1900	58.92	62.46	63.06	102.13	65.81	81.17
2000	62.41	66.10	66.72	108.32	69.65	86.24
2100	65.92	69.74	70.38	114.42	73.50	91.39
2200	69.43	73.34	74.01	120.57	77.32	96.62

TABLE 9 Enthalpy of various combustion gases at different temperatures