

Stoichiometric Calculations

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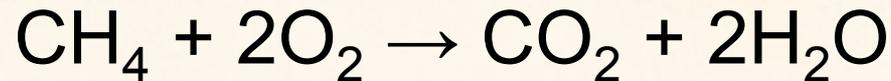
1. Applications of the Combustion Equation

- (1) Stoichiometric proportions for finding the correct air supply rate for a fuel
- (2) Composition of the combustion products is useful during the design, commissioning and routine maintenance of a boiler installation
- On-site measurements of flue gas composition and temperature are used as a basis for calculating the efficiency of the boiler at routine maintenance intervals.



2. Combustion Air Requirements: Gaseous Fuels

- Calculating the air required for gaseous fuels combustion is most convenient to work on a volumetric basis.
- The stoichiometric combustion reaction of methane is :



which shows that each volume (normally 1 m³) of methane requires 2 volumes of oxygen to complete its combustion.



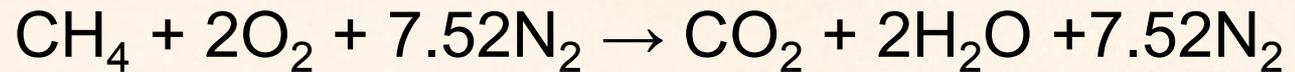
■ If we ignore the components which are present in the parts per million range, air consists of about 0.9% by volume argon, 78.1% nitrogen and 20.9% oxygen (ignoring water vapor). Carbon dioxide is present at 0.038%.

■ For the purposes of combustion calculations the composition of air is approximated as a simple mixture of oxygen and nitrogen:

| | |
|----------|-----|
| oxygen | 21% |
| nitrogen | 79% |



- The complete relationship for stoichiometric combustion:



as the volume of nitrogen will be
 $2 \times 79 \div 21 = 7.52$.

- A very small amount of nitrogen is oxidized but the resulting oxides of nitrogen (NO_x) are not formed in sufficient quantities to concern us here.

However, they are highly significant in terms of air pollution.



- It can be seen that the complete combustion of one volume of methane will require $(2+7.52=9.52)$ volumes of air, so the stoichiometric air-to-fuel (A/F) ratio for methane is 9.52.
- In practice it is impossible to obtain complete combustion under stoichiometric conditions. Incomplete combustion is a waste of energy and it leads to the formation of carbon monoxide, an extremely toxic gas, in the products.



 Excess air is expressed as a percentage increase over the stoichiometric requirement and is defined by:

$$\frac{\text{actual } A/F \text{ ratio} - \text{stoichiometric } A/F \text{ ratio}}{\text{stoichiometric } A/F \text{ ratio}} \times 100\%$$

 Excess air will always reduce the efficiency of a combustion system.



 It is sometimes convenient to use term excess air ratio, defined as:

$$\frac{\text{actual } A/F \text{ ratio}}{\text{stoichiometric } A/F \text{ ratio}}$$

 Where sub-stoichiometric (fuel-rich) air-to-fuel ratios may be encountered, for instance, in the primary combustion zone of a low-NO_x burner, the equivalence ratio is often quoted. This is given by:

$$\frac{\text{stoichiometric } A/F \text{ ratio}}{\text{actual } A/F \text{ ratio}}$$



3. Flue Gas Composition-Gaseous Fuels

- The composition of the stoichiometric combustion products of methane is:
1 volume CO_2
7.52 volumes N_2
2 volumes H_2O
- Given a total product volume, per volume of fuel burned, of 10.52 if water is in the vapor phase, or 8.52 if the water is condensed to a liquid. The two cases are usually abbreviated to “wet” and “dry”.



 The proportion of carbon dioxide in this mixture is therefore

$$\frac{1}{10.52} \times 100\% = 9.51\% \text{ wet} \quad \text{and}$$

$$\frac{1}{8.52} \times 100\% = 11.74\% \text{ dry}$$

 The instruments used to measure the composition of flue gases remove water vapor from the mixture and hence give a dry reading, so the dry flue gas composition is usually of greater usefulness.



Considering the combustion of methane with 20% excess air, the excess air (0.2×9.52) of 1.9 volumes will appear in the flue gases as $(0.21 \times 1.9) = 0.4$ volumes of oxygen and $(1.9 - 0.4) = 1.5$ volumes of nitrogen.

The complete composition will be:
constituent vol/vol methane

| | |
|------------------|------|
| CO ₂ | 1 |
| O ₂ | 0.4 |
| N ₂ | 9.02 |
| H ₂ O | 2 |

giving a total product volume of 12.42 (wet) or 10.42 (dry).



- The resulting composition of the flue gases, expressed as percentage by volume, is:

| Constituent (wet) | % vol (dry) | % vol |
|----------------------|-------------|-------|
| CO ₂ | 9.6 | 8.1 |
| O ₂ | 3.8 | 3.2 |
| N ₂ | 86.6 | 72.6 |
| H ₂ O | — | 16.1 |



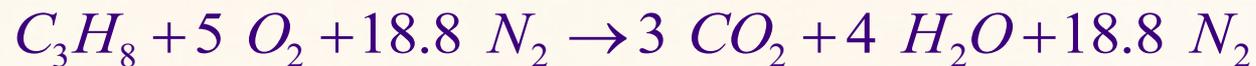
 Example 1:

A gas consists of 70% propane (C_3H_8) and 30% butane (C_4H_{10}) by volume. Find:

- (a) The stoichiometric air-to-fuel ratio and
- (b) The percentage excess air present if a dry analysis of the combustion products shows 9% CO_2 (assume complete combustion).

 Solution:

The combustion reactions for propane and butane are:



- (a) Stoichiometric Air Requirement
On the basis of 1 volume of the fuel gas, the propane content requires $0.7 \times (5 + 18.8) = 16.7$ vols air and the butane requires $0.3 \times (6.5 + 24.5) = 6.3$ vols air
Hence the stoichiometric air-to-fuel ratio is 23:1.



■ (b) Excess Air

The combustion products (dry) will contain

$$(0.7 \times 3) + (0.3 \times 4) = 3.3 \text{ vols CO}_2$$

$$(0.7 \times 18.8) + (0.3 \times 24.5) = 20.5 \text{ vols N}_2$$

plus u volumes excess air, giving a total volume of products of $(23.8 + u)$.

■ Given that the measured CO_2 in the products is 9%, we can write:

$$\frac{9}{100} = \frac{3.3}{(23.8 + u)}$$

hence $u = 12.87$ vols

■ The stoichiometric air requirement is 23 vols so the percentage excess air is:

$$\frac{12.87}{23} \times 100\% = 55.9\%$$



4. Combustion Air Requirements-Solid and Liquid Fuels

■ The way in which the combustion equation is used reflects the available information on the analysis of the solid or liquid fuels. This takes the form of an element-by-element analysis (referred to as an ultimate analysis) which gives the percentage by mass of each element present in the fuel.

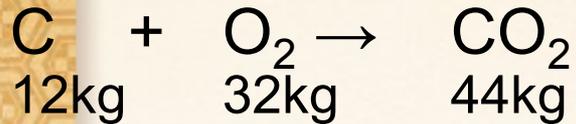
■ An example of an ultimate analysis of a liquid fuel (oil) might be :

| Component | % by mass |
|---------------------------|-----------|
| Carbon (C) | 86 |
| Hydrogen(H ₂) | 14 |



Each constituent is considered separately via its own combustion equation.

For the carbon:



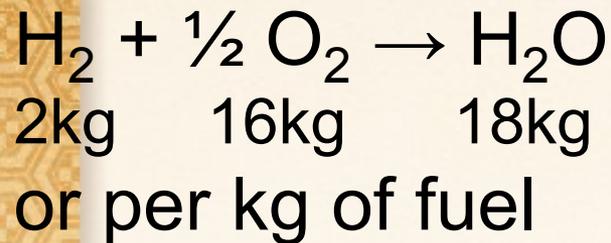
or for 1 kg of fuel

$$0.86 + 0.86 \times \frac{32}{12} \rightarrow 0.86 \times \frac{44}{12} \quad (\text{kg})$$

So each kg of oil requires 2.29 kg oxygen for combustion of its carbon and produces 3.15 kg CO₂ as product.



 Similarly



$$0.14 + 0.14 \times \frac{16}{2} \rightarrow 0.14 \times \frac{18}{2} \quad (\text{kg})$$

 In order to burn the hydrogen content of the oil 1.12 kg oxygen are needed and 1.26 kg water is formed.



 The total oxygen requirement is thus $(2.29 + 1.12)$ or 3.41 kg.

A given quantity of air consists of 21% by volume of oxygen.

$$\frac{6.72}{28.84} = 0.233$$

 We can simply transform to a mass basis thus:

| Component | vol fraction(vf) | vf × MW | Mass fraction |
|-----------|------------------|---------|---------------|
| Oxygen | 0.21 | 6.72 | |

| | | | |
|----------|------|--|--|
| Nitrogen | 0.79 | | |
|----------|------|--|--|

$$\frac{22.12}{28.84}$$

$$\frac{22.12}{28.84} = 0.767$$



 We can now establish that 3.41 kg oxygen, which is the stoichiometric requirement, will be associated with:

$$3.41 \times \frac{0.767}{0.233} = 11.23 \text{ kg nitrogen}$$

 The stoichiometric air-to-fuel ratio is thus $3.41 + 11.23 = 14.6 : 1$



5. Combustion Products-Solid and Liquid Fuels

■ The stoichiometric combustion products from combustion of the oil are:

| | |
|------------------|----------|
| CO ₂ | 3.15 kg |
| H ₂ O | 1.26 kg |
| N ₂ | 11.23 kg |

■ The combustion products would normally be needed as a volume percentage, so the reverse operation to that which was performed for air above is required.



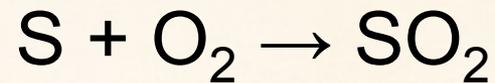
Hence if we require a dry volume percentage of the above products the following tabular procedure is convenient:

| Component | Mass/kg fuel | kmoles/kg fuel | mole fraction |
|-----------------|--------------|---|---------------|
| CO ₂ | 3.15 | $\frac{3.15}{44} = 0.0716$ | 0.151 |
| N ₂ | 11.23 | $\frac{11.23}{28} = 0.4011$ <hr/> 0.4727 | 0.849 |

The stoichiometric combustion products are thus 15.1% CO₂ and 84.9% N₂.



- Solid fuels, and many liquid fuels, contain compounds of sulfur. For the purposes of stoichiometric calculations this is assumed to burn to sulfur dioxide:



- In reality a mixture of sulfur dioxide and sulfur trioxide (SO_3) is produced, but it is conventional to assume combustion to SO_2 when calculating air requirements.



- Solid fuels and some oils produce ash when they burn. The percentage of ash in the fuel is part of the ultimate analysis and, as far as we are concerned at the moment, ash is simply treated as a totally inert substance.
- Many solid fuels contain small amounts of oxygen and nitrogen. The oxygen present in the fuel is considered to be available for burning the carbon, hydrogen and sulfur present. The nitrogen in the fuel is taken to appear as gaseous nitrogen in the combustion products.



■ Example 2: Combustion Calculation for a Coal
A coal has the following ultimate analysis:

| | % by mass |
|----------|-----------|
| Carbon | 90 |
| Hydrogen | 3 |
| Oxygen | 2.5 |
| Nitrogen | 1 |
| Sulfur | 0.5 |
| Ash | 3 |

Calculate:

- (a) the volumetric air supply rate required if 500 kg/h of coal is to be burned at 20% excess air and
- (b) the resulting %CO₂ (dry) by volume in the combustion products.



 Solution:

Lay out the calculation on a tabular basis using 1 kg coal:

| | Mass (per kg) | O ₂ Required | Products |
|----------|---------------|--------------------------------------|-------------------------------------|
| Carbon | 0.9 | $0.9 \times \frac{32}{12} = 2.4$ | $0.9 \times \frac{44}{12} = 3.3$ |
| Hydrogen | 0.03 | $0.03 \times \frac{16}{2} = 0.24$ | $0.03 \times \frac{18}{2} = 0.27$ |
| Sulfur | 0.005 | $0.005 \times \frac{32}{32} = 0.005$ | $0.005 \times \frac{64}{32} = 0.01$ |
| Oxygen | 0.025 | -0.025 | - |
| Nitrogen | 0.01 | - | 0.01 |
| Ash | 0.03 | - | - |



 (a) Oxygen required to burn 1 kg coal = 2.4 + 0.24 + 0.005 - 0.025 = 2.62 kg.

$$\text{Air required} = \frac{2.62}{0.233} = 11.25 \text{ kg}$$

$$\text{Actual air supplied} = 11.25 \times 1.2 = 13.5 \text{ kg}$$

Assuming a density for air of 1.2 kg/m³, the flow rate will be:

$$13.5 \times \frac{500}{1.2 \times 3600} = 1.56 \text{ m}^3/\text{s}$$



- (b) To get the %CO₂ in the combustion products we need to know the amounts of oxygen and nitrogen in the flue gases.

Air supplied = 13.5 kg per kg coal, of which oxygen is

$13.5 \times 0.233 = 3.14$ kg, and nitrogen

$13.5 - 3.14 = 10.36$ kg.

- The combustion products will thus contain:

$3.14 - 2.62 = 0.52$ kg O₂ and

$10.36 + 0.01 = 10.37$ kg N₂.





A second tabular procedure can now be used for the volumetric composition of the flue gases:

| Product | Mass/kg coal | Mol. Wt. | kmoles/kg coal | %volume |
|-----------------|--------------|----------|----------------|----------------------|
| CO ₂ | 3.3 | 44 | 0.075=(3.3/44) | 16.25=(0.075/0.4614) |
| SO ₂ | 0.01 | 64 | 0.000156 | 0.03 |
| O ₂ | 0.52 | 32 | 0.0162 | 3.51 |
| N ₂ | 10.37 | 28 | <u>0.37</u> | 80.20 |
| | | | 0.4614 | |



6. Practical Significance of the Flue Gas Composition

- It is comparatively easy to make on-site measurements of the dry volumetric concentration of either carbon dioxide or oxygen in the flue gases.
- Either of these measurements can be used to calculate the air-to-fuel ratio (or excess air) if the composition of the fuel is known and the combustion of the fuel is complete.
- The volume percentage of oxygen or carbon dioxide in the flue gas will be influenced by the level of excess air and also by the carbon:hydrogen ratio present in the fuel.



■ If pure carbon is burnt, the only combustion product is carbon dioxide, so each molecule of oxygen in the combustion air becomes a molecule of carbon dioxide in the flue gas. This means that the stoichiometric combustion of carbon will produce 21% by volume CO₂.

■ If we consider for the moment that hydrocarbon fuels consist only of carbon and hydrogen, as the carbon:hydrogen ratio of the fuel decreases the stoichiometric air-to-fuel ratio will increase.

This is because 1 kg carbon requires $32/12=2.67$ kg of oxygen for complete combustion but 1 kg hydrogen requires 8 kg oxygen.



- The percentage CO_2 in the flue gases will fall as the carbon:hydrogen ratio in the fuel decreases as
 - (1) less carbon dioxide will be produced per kilogram of fuel and
 - (2) the increased air requirement means that the carbon dioxide produced will be diluted by the extra nitrogen in the flue gas.
- This effect is illustrated in Table 2.1 ([next slide](#)). The carbon:hydrogen ratio in fuels lie between the limits of 75:25 (methane) to around 95:5 ([high carbon coals](#)).



Table 2.1 Carbon dioxide concentraton in flue gases

| C : H (by mass) | | Satoichiometric %CO ₂ |
|-----------------|----|----------------------------------|
| 100 | 0 | 21.00 |
| 95 | 5 | 18.67 |
| 90 | 10 | 16.62 |
| 85 | 15 | 14.81 |
| 80 | 20 | 13.19 |
| 75 | 25 | 11.73 |
| 70 | 30 | 10.42 |
| 65 | 35 | 9.23 |



- Next slide ([Fig. 2.1](#))
There is a unique relationship between the composition of the flue gas and the excess air for any [given fuel](#).



Constituent % by vol.

| | |
|---|------|
| CH ₄ | 92.6 |
| C ₂ H ₆ | 3.6 |
| C ₃ H ₈ | 0.8 |
| C ₄ H ₁₀ | 0.2 |
| C ₅ H ₁₂ (and higher) | 0.1 |
| CO ₂ | 0.1 |
| N ₂ | 2.6 |

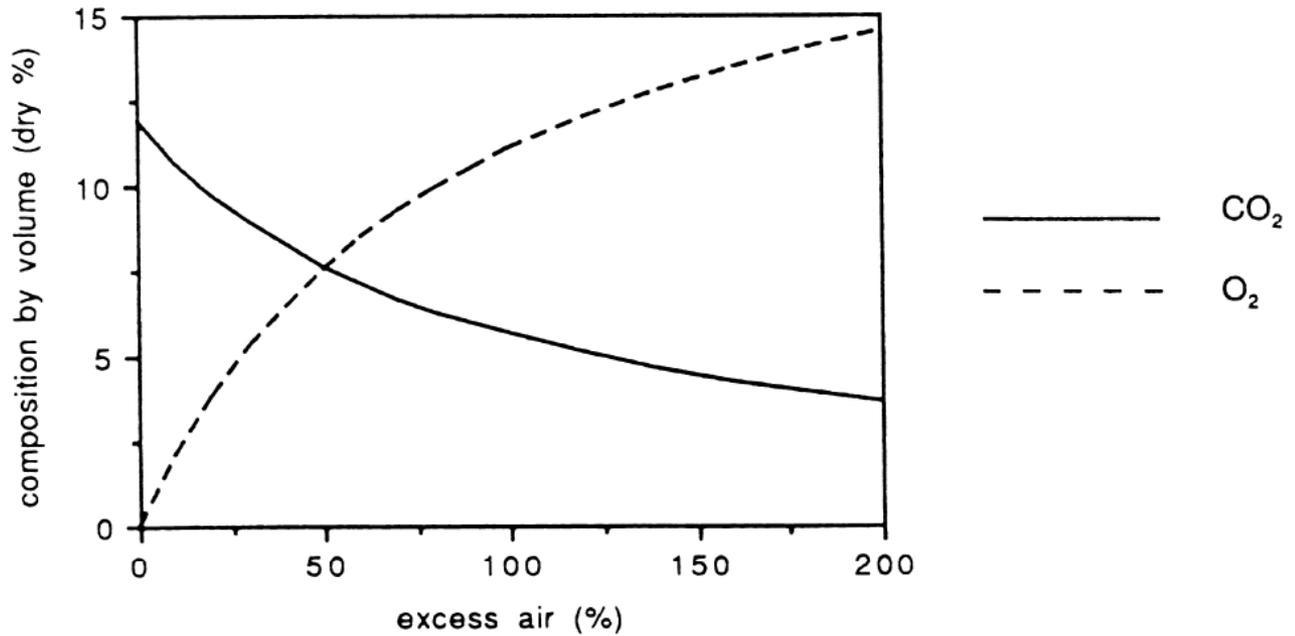


Figure 2.1 Flue gas composition for natural gas

Next Slide ([Fig. 2.2](#))

A plot of the percentage CO_2 in the flue gases over a range of values of excess air for C:H ratios ranging from 75:25 to 95:5.

The curves for fuels with higher C:H ratios lie above those for fuels with a lower value of [this ratio](#).



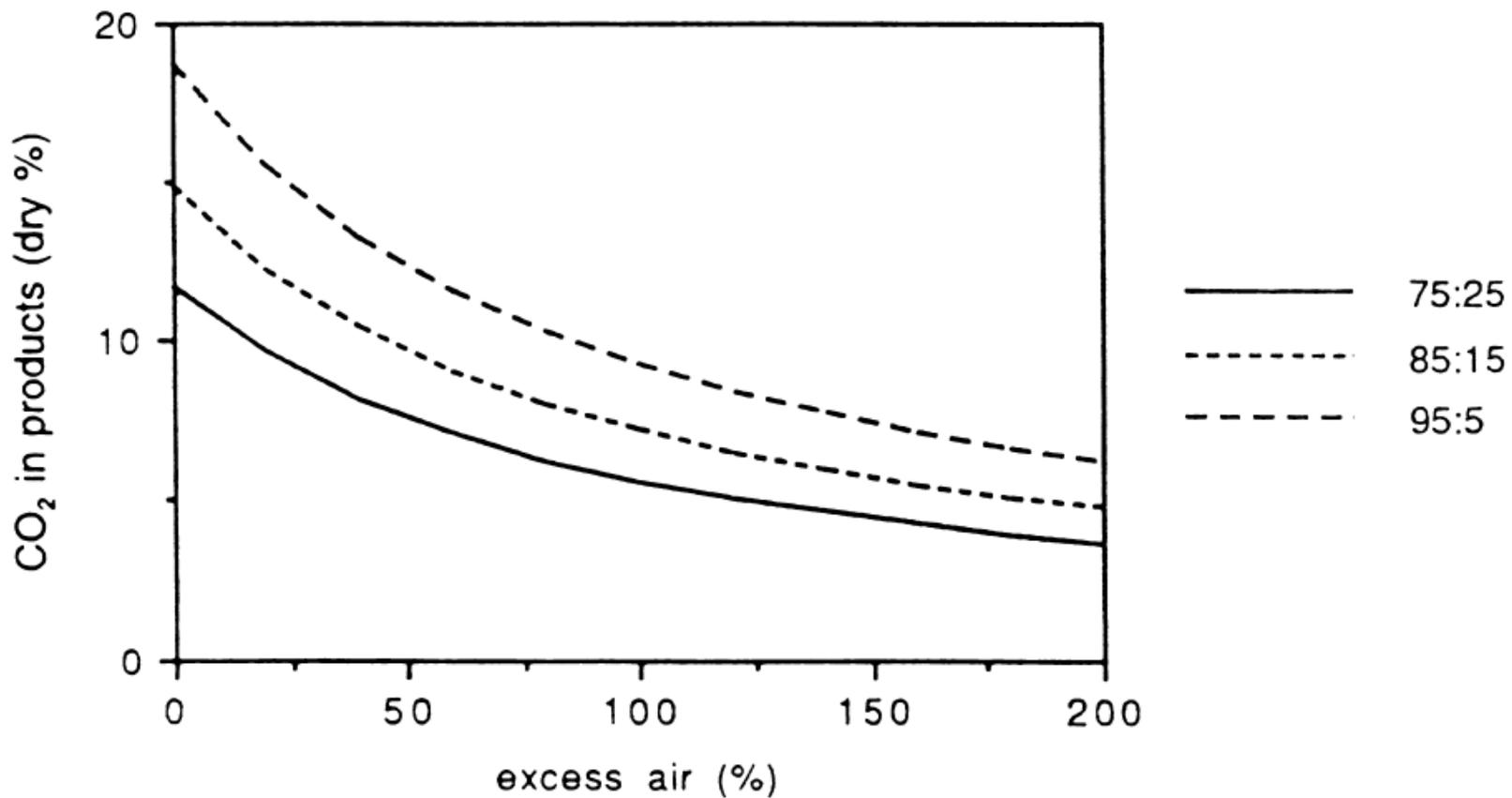


Figure 2.2 Carbon dioxide in combustion products

Next Slide ([Fig. 2.3](#))

The relationship between the percentage oxygen in the flue gas and the excess air is very similar for a wide range of fuels.

This is different from the [CO₂ curves](#).



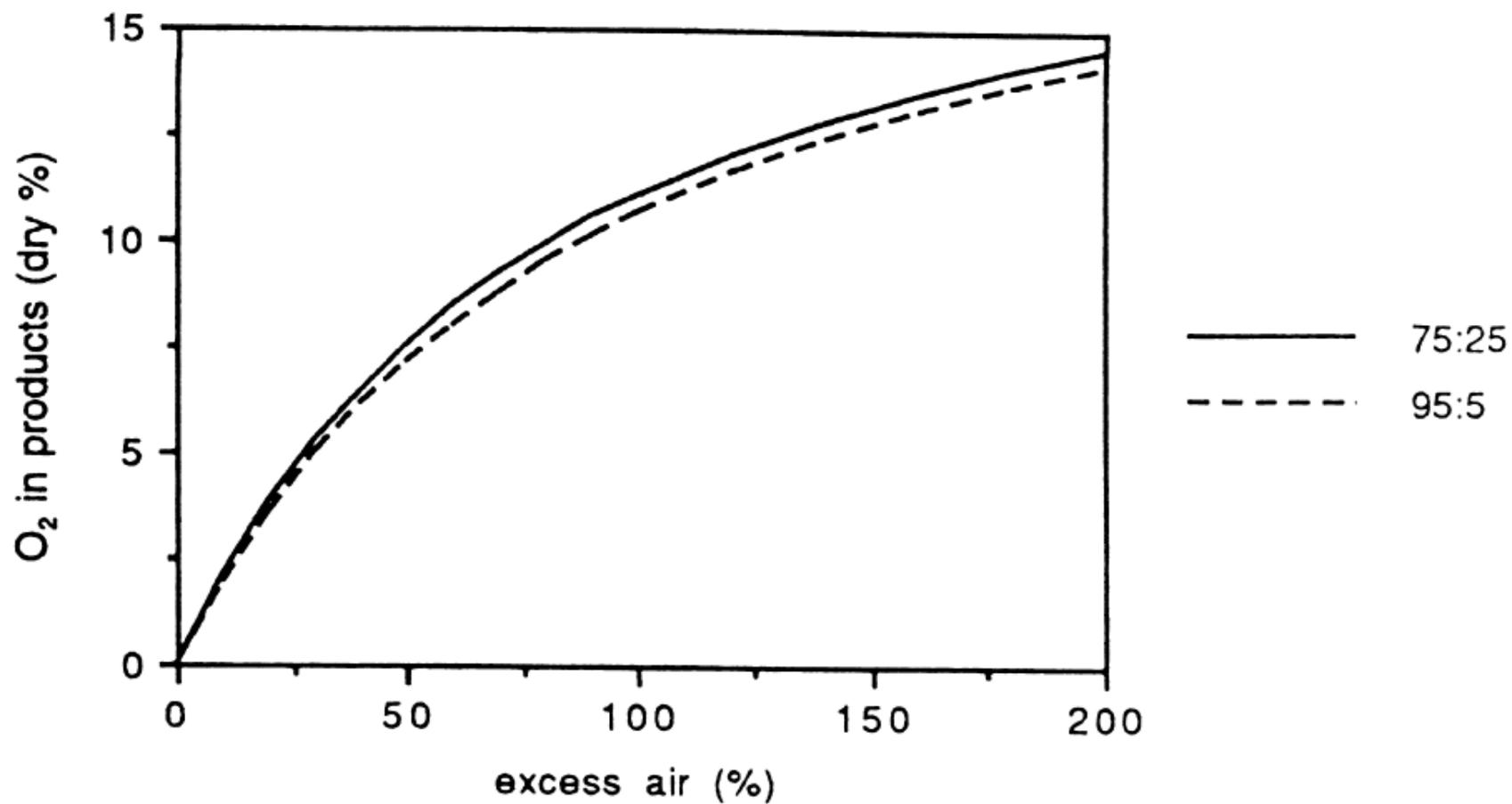
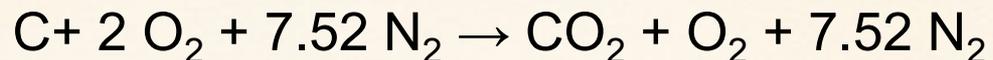


Figure 2.3 Oxygen in combustion products

Take the combustion of two “extreme” cases: one kmole of carbon and one kmole of methane. In each case we will consider 100% excess air.

The combustion of carbon under these conditions is described by:



The percentage of oxygen in the flue gas is thus:

$$[1/(1+1+7.52)] \times 100\% = 10.5\%$$

The corresponding equation for methane is



giving a percentage oxygen of

$$[2/(1+2+15.05)] \times 100\% = 11\%$$



7. Sub-stoichiometric Combustion

- There are circumstances in which localized fuel-rich combustion can take place, such as where combustion of the fuel is a two-stage process with secondary air added downstream of the primary combustion zone.
- The mechanism of combustion of a fuel with less than the stoichiometric air requirement consists of the following sequence of events:
 - (1) The available oxygen firstly burns all the hydrogen in the fuel to water vapor.
 - (2) All the carbon in the fuel is then burned to carbon monoxide.
 - (3) The remaining oxygen is consumed by burning carbon monoxide to carbon dioxide.



Next slide ([Fig. 2.4](#))

It can be seen that as the air supply falls below the stoichiometric requirement the percentage of carbon monoxide in the flue gas increases [very quickly](#).



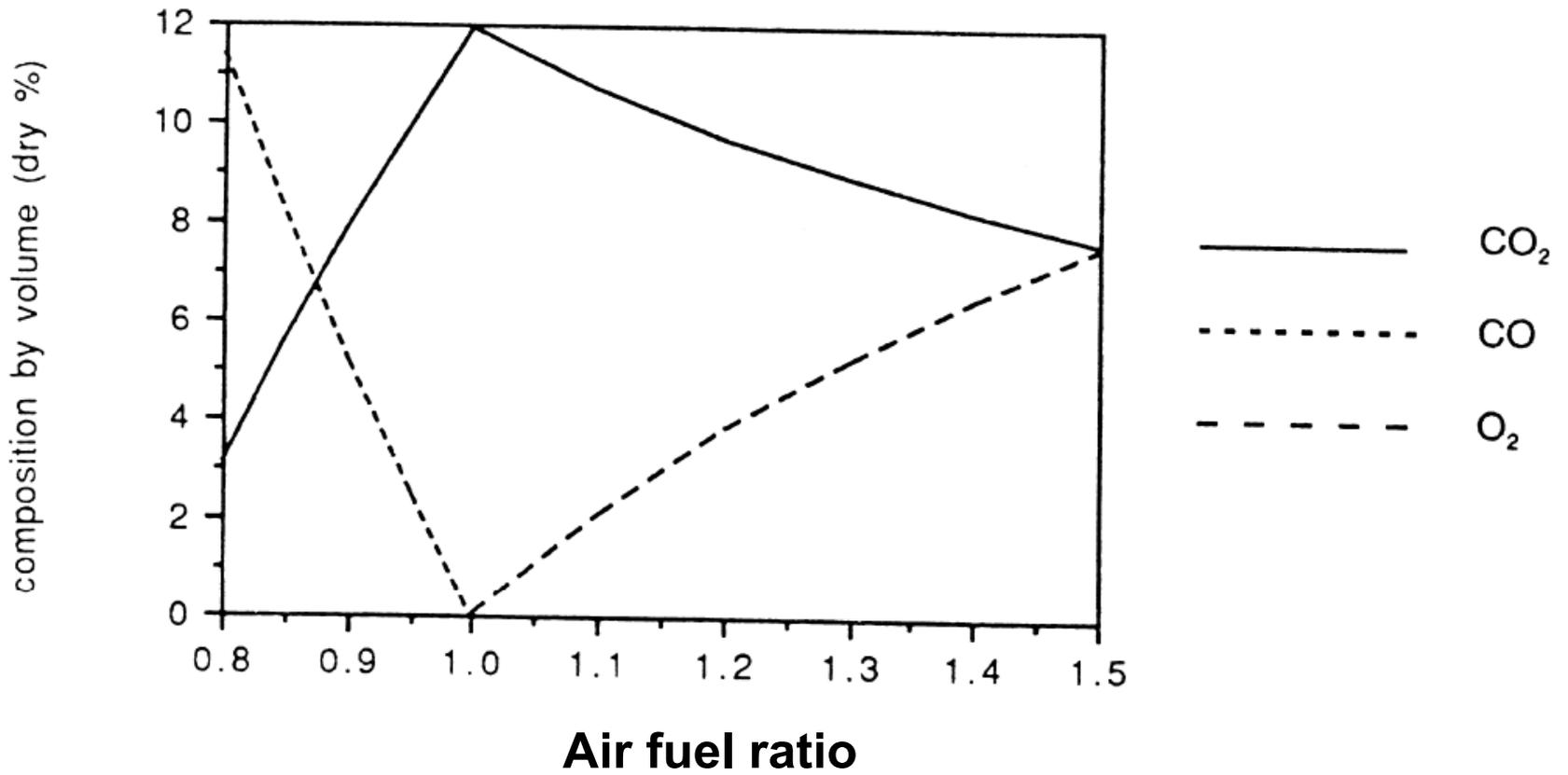
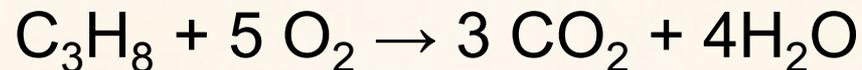


Figure 2.4 Sub-stoichiometric combustion of natural gas

- Example 3: Combustion of a Fuel under Sub-Stoichiometric Conditions
Estimate the wet and dry flue gas composition if propane is burned with 95% of the stoichiometric air requirement.

- Solution:**

the stoichiometric reaction for this fuel is



On a volumetric basis we have $(5 \times 0.95)=4.75$ volumes of O_2 available. This means that the accompanying nitrogen is 17.87 volumes.



- Firstly all the hydrogen in the fuel is burned to water. This will produce 4 volumes of water vapor and consume 2 volumes of oxygen, leaving 2.75 volumes for further combustion of the carbon in the fuel.
- We assume that all the carbon initially burns to carbon monoxide and then the remaining oxygen is used in burning the carbon monoxide to carbon dioxide.



■ Burning the carbon to CO will produce 3 volumes of CO and use up 1.5 volumes of oxygen, leaving $(2.75-1.5)=1.25$ volumes of oxygen for further combustion.

■ Next reaction is



So 1.25 volumes oxygen can burn 2.5 volumes of carbon monoxide, producing 2.5 volumes of carbon dioxide.

■ The remaining carbon monoxide is therefore $(3-2.5)=0.5$ volume.



■ The products of combustion are thus:

| | |
|------------------|---------------|
| N ₂ | 17.87 volumes |
| CO | 0.5 |
| CO ₂ | 2.5 |
| H ₂ O | 4.0 |

| | |
|-------|-------|
| Total | 24.87 |
|-------|-------|

■ Giving the percentage compositions:

| | Wet(%) | Dry(%) |
|------------------|--------|--------|
| N ₂ | 71.9 | 85.6 |
| CO | 2.0 | 2.4 |
| CO ₂ | 10.0 | 12.0 |
| H ₂ O | 16.1 | - |

