

BUDAPEST UNIVERSITY OF TECHNOLOGY  
AND ECONOMICS  
Faculty of Mechanical Engineering



DEPARTMENT OF ENERGY ENGINEERING

# Combustion

## Heat Engines and Boilers

Lecture note for the undergraduate BSc course

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## I. COMBUSTION

Combustion is one of the important energy-conversion process, in which the energy in a fuel is released by an exothermic chemical reaction.

Life and comfort needs more and more energy

Sustainable development needs large efforts

Less energy and fuel consumption for the same comfort.

Energy generation in environmental friendly way, with little environmental pollution.

### **Fuels, fuel technology**

Fuel classification:

State of matter	Fossil (Result of long term decomposition and accumulation)	Renewable (It can be produced from year to year or from decade to decade)
Solid materials)	Coal	Biomass: wood, cane, grass, etc. (Energy plants or waste
Liquid	Crude Oil Petrol, Kerosene, Diesel Oil	Bio-Ethanol Vegetable oil (biodiesel)
Gaseous	Natural gas	Bio-gas Digester gas, pyrolysis-gas

These fuels can be delivered, stored and burned at different power level  
According to energy demands

Energy content	High	Low
Delivery	even for long distance	only for short distance
Storage capacity	small	large
Other renewables:	Solar, wind, tidal energy	depends on weather conditions Can not be stored
	Hydro-, geothermal power	depends on geographical conditions

Most of fuels can be burned, but what is burning, or combustion?

Do you know the camp-fire, or a fire place in a dining room?

At the bottom there are laid small peaces, over it bigger ones and it is ignited by a newspaper. The difficulty of trying to burn a single lag is well known, but a number of lags can be ignited easily.

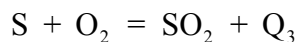
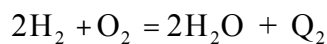
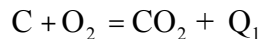
What do you think is the reason of this?

The right answer is, that through preheating the woodpeaces distillation of volatile matter takes place.

What is volatile matter - gaseous hydrocarbons.

The chemical reaction requires a source of oxygen for combustion to take place and this is usually air.

The combustion is simply said the reaction process of Carbon or Hydrogen (these are must important fuel elements) with Oxygen



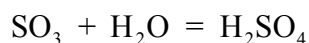
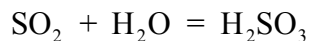
$Q_1, Q_2, Q_3$  represent the heat evolving from the reactions.

These are called exotherm reactions because they produce heat.

Reactions which need heat are called endotherm reactions.

Although sulphur oxidation produces heat, but it causes also difficulties.

In further reactions sulphur oxides with water can produce different types of sulphur acid, which can cause corrosion and acid rain.



But what is easy for a chemist, is not easy for an engineer.

The engineer has to realise the process in industrial size, but he knows, that reactions take place only at micro level.

In practical engines and power plants the source of heat is the chemical energy of substances called fuels. This energy is released during the chemical reaction of the fuel with oxigen. The fuel elements combine with oxygen is an oxidation process which is rapid and is accompanied by the evolution of heat.

Combustion technology is the science of how to burn fossil fuel under industrial circumstances.

But to do this, it is necessary to recognize the fossil fuels.

The chemical composition of fossil fuels (percentage by weight, average values):

	C	H	O	N	S
Wood	50	6	43	0.5	0.5
Lignite	70	5	23	1	1
Anthracite	94	3	1	1	1
Crude oil	86	13	-	-	1
Natural gas	75	24.5	-	0.5	-

### Coal:

Coal represents the largest fossil-fuel energy resource in the world.

New combustible fuel options include the so-called synthetic fuels, or synfuels, which are liquids and gases derived largely from coal, oil shale, and tar sands. A tiny fraction of fuels used today are industrial by-products, industrial and domestic wastes, and biomass

There are many ways of classifying coal according to its chemical and physical properties. The most accepted system is the one used by the American Society for Testing and Materials (ASTM)

### Classification of coal:

The most general classification divides coal into lignites, bituminous and anthracite coals, in which the basis of classification is age.

### Lignites:

It may be black or brown and earthy, with a woodlike structure. Very often it has a high moisture and volatile matter content. It has a low calorific value about 8 - 15 MJ/kg.

In our country, in Hungary the available lignite has very low calorific value, which is only 6 - 8 MJ/kg.

Physical properties of coal, in the assessment of different types of coal for industrial purposes:

	Moisture [%]	Ash [%]	Volatile matter [%]	Calorific value [MJ/kg]
Lignite	20 - 40	7 - 12	40 - 50	21 - 29
Bituminous	5 - 15	2 - 10	20 - 45	32 - 33
Anthracite	2 - 3.5	1 - 2	7 - 9	35 - 36

More precise classification is based upon chemical composition but in addition coal are separated according to their size and ash content.

### Solid fuel analysis

#### Ultimate analysis

An accurate chemical analysis by mass of the important elements in the fuel is called ultimate analysis.

The solid and liquid fuels consist of the following elements: carbon (C), hydrogen (H), nitrogen (N), oxygen (O). In addition to these elements -- which form the organic matter--the fuels contain undesirable pollutants as well. These are: the sulphur (S), ash (a) and water or moisture (mt). The letter shown in brackets denote not only the components, but their mass too, in percentage of the fuel.

$$C + H + N + O + S + a + mt = 100\%.$$

Burnable elements in the fuel are carbon, hydrogen and partly sulphur.

The amount of heat generated during burning of 1 kg fuel depends mainly on the carbon and hydrogen content.

The burnable part of the sulphur separates in the form of gas and it is called burnable sulphur (S<sub>b</sub>) The non-burnable sulphur remains in the ash

Composition of the fuel is frequently given without taking into account the ash and moisture content. The standard name of this composition is the burnable mass, though the oxygen and nitrogen included in this composition are non-burnable elements.

$$C + H + N + O + S = 100\%$$

Presence of the moisture and ash in the fuel is not desirable because these form the non-burnable part (ballast). But a small part of moisture is good for burning process.

A certain part of the sulphur too is classified as such. The SO<sub>2</sub> and SO<sub>3</sub> produced during burning of the remaining part of the sulphur are detrimental to the metal part of the boiler and to the surroundings of the power plant. The carbon content of the various solid fuels calculated to the burnable mass is 90-95%, the hydrogen 1-6%, and the sulphur 0-8%.

Ultimate analysis is needed for burning calculation. (stoichiometric calculation)

Proximate analysis

Another analysis of coal, which is called the proximate analysis gives a percentages of moisture, volatile matter, combustible solid (called fix carbon), and ash.

Basic method for this analysis is given by ANSI/ASTM Standard D 3172

- fix carbon      - combustible solid
- volatile matter - Total volatile mass is the product in the state of gas and steam except the analytical moisture-which emerges from the brown coal during heating at  $850 \pm 25^\circ\text{C}$  in air-tight space.  
Burnable volatile is calculated on the basis of the standard specifications, which does not contain incombustible parts listed in the following.  
Incombustible volatile is the part of the total volatile mass which contains the hydrate and crystal water of inorganic origin, carbonate carbon dioxide of inorganic origin and decomposed carbon dioxide of organic origin,
- moisture      - Total moisture is the water content of the coal without the so-called constitutional water.  
Constitutional water is the crystal and hydrate water of inorganic origin, and the decomposed water of organic origin, liberated and occurring at a temperature over  $140^\circ\text{C}$ .
- ash              - is the inorganic salts contained in coal.

Proximate analysis is needed for designing burners and boilers.

**Composition of solid fuels,  
and analysis methods**

Original substance	Green coal, damp wood, waste in original state									
General composition	Combustible					Incombustible, ballast				
						Mineral matter		Moisture, or Water content		
Drying at ambient air	Air-dry fuel									Free or surface moisture,
Drying at 105 °C	Water free fuel					Hygroscopic moisture				
	Combustible			Incombustible						
Heating at 850 °C without air	Volatile matter					Coke residue		Total moisture, Water content (w)		
Complete combustion at 850°C						Fix Carbon (fixC)	Ash (a)			
Result: Proximate analysis										
Ultimate analysis	Sulfur (S)	Nitrogen (N)	Oxygen (O)	Hydrogen (H)	Total Carbon (C)					

## Crude oil

The hydrocarbon components in crude oil are made up of paraffins, naphthens and aromatics. Crude oil is broken up into fractions by distillation.

Analysis data of liquid fuels:

	Symbol	Unit	Benzine (standard)	Petroleum/ kerosine	Gas oil EL	Residual oil (S = 2,3%)	Residual oil (S = 1,0%)	Coal tar fuel "Z"	Coal tar fuel "M"			
Properties												
Higher calorific value	H <sub>o</sub>	kWh/kg	13,15	12,85	12,70	12,04	12,50	10,84	11,15			
	H <sub>o</sub>	MJ/kg	47,33	46,27	45,73	43,33	45,00	39,03	40,15			
	H <sub>o</sub>	Mcal/kg	11,30	11,05	10,92	10,35	10,75	9,32	9,59			
Lower calorific value	H <sub>u</sub>	kWh/kg	12,28	12,00	11,89	11,36	11,83	10,42	10,69			
	H <sub>u</sub>	MJ/kg	44,20	43,20	42,81	40,91	42,60	37,70	38,50			
	H <sub>u</sub>	Mcal/kg	10,56	10,32	10,22	9,77	10,18	8,96	9,20			
Density at 15°C	ρ	g/ml	0,73	0,81	0,84	0,95	0,96	1,05	1,08			
Flash point	ϑ <sub>F</sub>	°C	> 21	> 40	> 55	> 65	> 65	> 90	> 90			
Viscosity at 20°C at 50°C at 100°C	ν	mm <sup>2</sup> /s	0,7	1,8	5,0	—	—	5,1	—			
	ν	mm <sup>2</sup> /s	—	—	2,6	ca. 300	ca. 300	2,6	ca. 30			
	ν	mm <sup>2</sup> /s	—	—	—	ca. 30	ca. 30	—	ca. 6,5			
Combustion quantities (for λ = 1)												
Air requirement	V <sub>L</sub>	m <sup>3</sup> /kg	11,42	11,33	11,24	10,57	10,62	9,79	10,02			
Dry flue gas volume	V <sub>A dry</sub>	m <sup>3</sup> /kg	10,62	10,54	10,49	9,98	10,04	9,44	9,77			
Wet flue gas volume	V <sub>A, f</sub>	m <sup>3</sup> /kg	12,12	12,02	11,89	11,14	11,19	10,17	10,55			
Water content in flue gas	H <sub>2</sub> O <sub>D</sub>	kg/kg	1,28	1,26	1,20	0,99	0,98	0,62	0,67			
Max. carbon dioxide	CO <sub>2</sub> max	Vol.-%	14,94	14,99	15,25	15,83	15,99	18,0	18,1			
Composition												
Carbon	C	% Wt.	85,6	85,3	86,3	85,2	86,6	91,0	91,6			
Hydrogen	H	% Wt.	14,35	14,1	13,4	11,1	11,0	6,5	7,0			
Sulphur	S	% Wt.	0,05	0,2	0,3	2,3	1,0	0,5	0,3			
Oxygen	O <sub>2</sub>	% Wt.	—	0,3	—	1,0	1,0	1,4	0,7			
Nitrogen	N <sub>2</sub>	% Wt.	—	0,1	—	0,3	0,3	0,5	0,3			
Water	H <sub>2</sub> O	% Wt.	—	—	—	0,1	0,1	0,1	0,1			
Total	Σ	% Wt.	100	100	100	100	100	100	100			
Combustion of sulphur and elementary fuels			H <sub>o</sub> MJ	H <sub>u</sub> MJ	Requirement O <sub>2</sub> m <sup>3</sup>	Air m <sup>3</sup>	Combustion products N <sub>2</sub> : m <sup>3</sup>		Flue gas quantity dry m <sup>3</sup>		Values for emission calculation	
1 kg pure carbon — burnt to CO <sub>2</sub> — burnt to CO	C		33,83	33,83	1,86	8,90	7,03	CO <sub>2</sub> : 1,85	8,89	—	20,85 Vol.-% CO <sub>2</sub> max 1,17 kg CO	
			10,10	10,10	0,93	4,45	3,52	CO : 0,93	4,45	—		
1 kg pure hydrogen	H		141,80	119,97	5,55	26,51	20,96	H <sub>2</sub> O <sub>D</sub> : 10,47	20,96	31,42	8,94 kg H <sub>2</sub> O <sub>D</sub>	
1 kg pure sulphur	S		9,25	9,25	0,70	3,33	2,63	SO <sub>2</sub> : 0,68	3,32	—	2,00 kg SO <sub>2</sub>	

Fig. 1.  
Composition and features of different liquid fuels

Important physical properties of liquid fuels are:

### Viscosity

Viscosity of the oil is characteristic to the internal friction of the liquid, which is one of the most important characteristics from the firing technical point of view. The viscosity is characterized with physical and technical measuring units. Since the SI measuring unit has not been taken over in the practice in respect of this characteristic, thus both measuring units are introduced:

$$\begin{array}{ll} \eta \text{ dynamic viscosity: [Ns/m}^2\text{]} & 1 \text{ cP} = 10^{-3} \text{ Pa s} \\ \nu \text{ kinematic viscosity: [m}^2\text{/s]} & 1 \text{ cSt} = 10^{-6} \text{ m}^2\text{/s} \end{array}$$

$$\eta = \rho \cdot \nu$$

The kinematic viscosity in the technical practice may be given in arbitrarily chosen units, in Engler degrees (°E) and Redwood units too, and the conversions can be carried out with empirical relationships.

Engler viscosity:

$$E^{\circ} = \frac{\text{running out time of } 200 \text{ cm}^3 \text{ oil at } t^{\circ} \text{ C temperature}}{\text{running out time of } 200 \text{ cm}^3 \text{ water at } 20^{\circ} \text{ C temperature}}$$

The viscosity of the oil depends on the temperature to a great extent, the kinematic viscosity declines exponentially with the rise of the temperature.

For comparison of the different kinematic viscosity units some identical viscosity conditions are shown in the enclosed diagram.

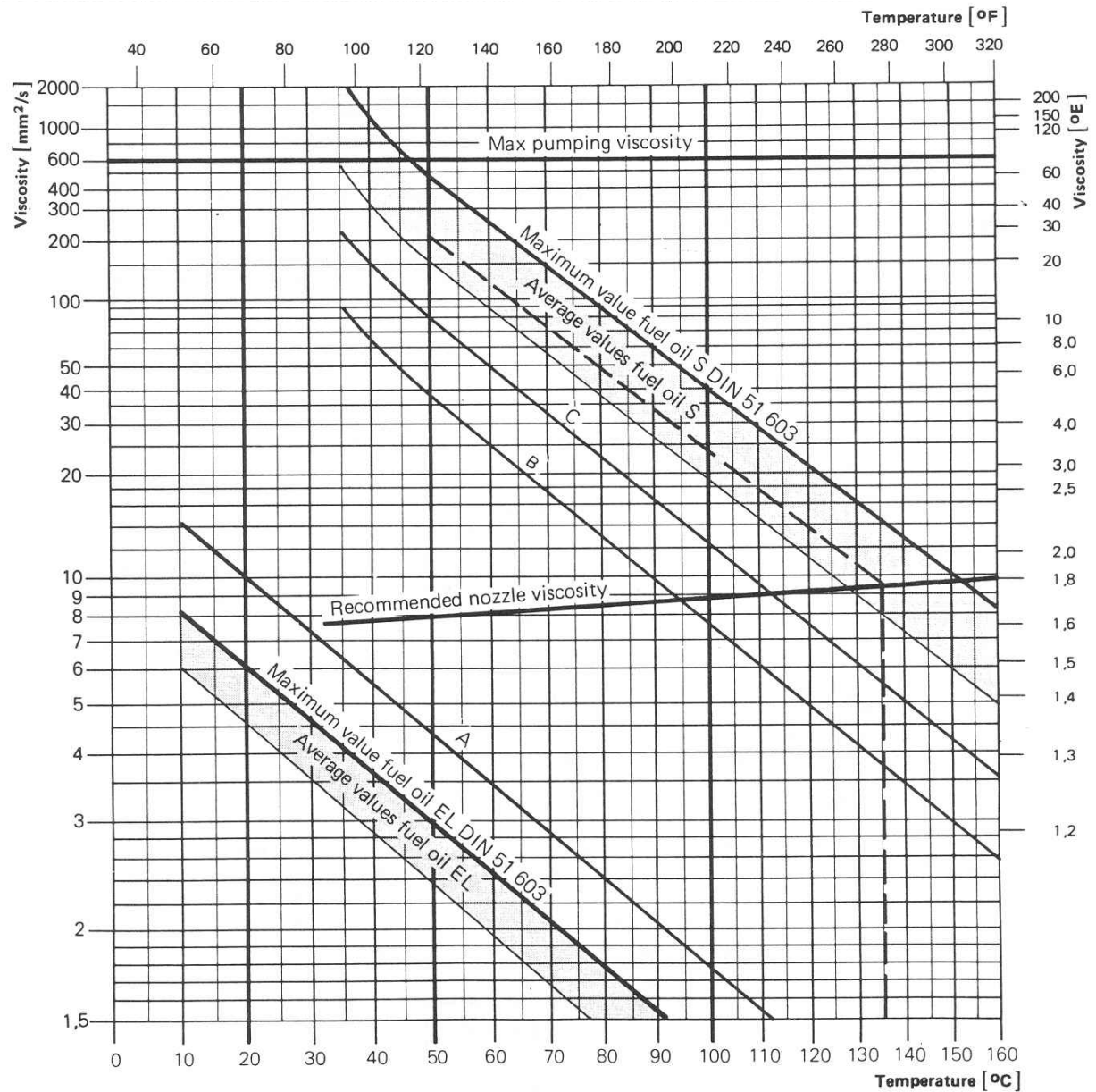


Fig.2.  
Viscosity variation of different fuel oils

### Point of solidification

The point of solidification is understood as the temperature at which the crude oil product no longer flows upon the effect of the gravitational force. Its value is significant first of all in respect of transportation.

### Flash point

Flash point is the temperature at which as much vapour generates from the crude oil product under the pressure of 0.101 MPa that, mixed with the ambient air, upon approach of flame it flashes over the whole oil surface.

### Ignition point, boiling point

Burning of the oil-discussed later-occurs after transition into the vapour phase, hence knowledge of the boiling point of the oil is essential. The oil below the temperature of the boiling point can not burn. The ignition point is always higher than the boiling temperature. The boiling temperature of the oils depends on the composition.

Ignition point is the temperature at which the self-ignition of the fuel vapour takes place, while the just generated heat exceeds the amount of heat transferred to the surroundings and thereby it maintains the burning for at least 5 s. The ignition point does not characterize unequivocally the inflammability of the oil.

### Firing point

Firing point is the temperature at which vaporization of the liquid is of such extent, that with the approach of the flame for a short time it is ignited and the burning will be constant on the surface. The firing point is characteristic to the inflammability of the fuel.

### Conradson number

The liquid fuel is heated and vaporized in an air-tight vessel, then the oil vapour is burnt up. During heating a certain part of the hydrocarbon compounds is decomposed and retained with other components. The retained coke part related to the initial amount of oil gives the Conradson number. The coking is an important characteristic first of all of the evaporator type burner, but it is characteristic to the coking of other burners too.

Gasous fuels

Gasous fuels are chemically the simplest of the three groups.

The natural gas is the mixture of various gases. Its composition depends on the site, but their properties are not very different from one another.

"Natural gas" is used for gasous fuels which occurs naturally and is burned after a minimum of treatment or processing.

Typical composition of natural gas is

CH <sub>4</sub>	85%
C <sub>2</sub> H <sub>6</sub>	10%
C <sub>3</sub> H <sub>8</sub>	3%

The major nonhydrocarbon constituents are CO<sub>2</sub>, N<sub>2</sub>, He and H<sub>2</sub>S

H<sub>2</sub>S is corrosive, toxic and has a foul odour.

Natural gas are liquefied for distribution by tanker and for use as liquid fuels.

LNG - liquid natural gas (consisting mainly methane)

LPG - liquified petroleum gas ( consisting mainly propane and butane)

Properties of different burnable gases are shown in the enclosed table. [See page 9.]

	Symbol	Unit	Natural gas L	Natural gas H	Natural gas L/ Air 1)	Propane / Air 2)	Butane / Air 3)	Towns gas
<b>Properties</b>								
Higher calorific value	H <sub>o</sub>	kWh/m <sup>3</sup>	9,78	11,46	6,14	7,49	7,52	5,51
	H <sub>o</sub>	MJ/m <sup>3</sup>	35,21	41,26	22,10	26,95	27,08	19,82
	H <sub>o</sub>	Mcal/m <sup>3</sup>	8,41	9,85	5,28	6,44	6,47	4,73
Lower calorific value	H <sub>u</sub>	kWh/m <sup>3</sup>	8,83	10,35	5,54	6,89	6,95	4,89
	H <sub>u</sub>	MJ/m <sup>3</sup>	31,77	37,26	19,94	24,82	25,01	17,59
	H <sub>u</sub>	Mcal/m <sup>3</sup>	7,59	8,90	4,76	5,93	5,97	4,201
Inflammability limits (% Vol. gas in air, at 20°C)								
Lower inflammability limit	Z <sub>u</sub>	% Vol.	5	4	7	7,5	7,5	5
Higher inflammability limit	Z <sub>o</sub>	% Vol.	15	16	20,5	36	42	30
Wobbe Index (related to H <sub>o</sub> )	W <sub>o</sub>	kWh/m <sup>3</sup>	12,21	14,72	6,98	6,98	6,82	8,74
	W <sub>o</sub>	MJ/m <sup>3</sup>	43,97	53,00	25,14	25,14	24,54	31,46
	W <sub>o</sub>	Mcal/m <sup>3</sup>	10,50	12,66	6,00	6,00	5,86	7,51
Wobbe Index (related to H <sub>u</sub> )	W <sub>u</sub>	kWh/m <sup>3</sup>	11,02	13,29	6,30	6,43	6,29	7,75
	W <sub>u</sub>	MJ/m <sup>3</sup>	39,68	47,85	22,68	23,15	22,66	27,91
	W <sub>u</sub>	Mcal/m <sup>3</sup>	9,48	11,43	5,42	5,53	5,41	6,67
Density	ρ	kg/m <sup>3</sup>	0,829	0,784	1,000	1,486	1,575	0,513
relative density	d	—	0,641	0,606	0,773	1,149	1,218	0,397
<b>Combustion values</b> (for λ = 1)								
Air requirement	V <sub>L</sub>	m <sup>3</sup> /m <sup>3</sup>	8,45	9,91	4,93	5,75	5,74	4,33
Dry flue gas volume	V <sub>A,tr</sub>	m <sup>3</sup> /m <sup>3</sup>	7,72	8,90	4,85	5,94	6,00	3,91
Wet flue gas volume	V <sub>A,f</sub>	m <sup>3</sup> /m <sup>3</sup>	9,37	10,82	5,88	6,96	7,00	4,98
max. carbon dioxide	CO <sub>2 max</sub>	% Vol.	11,65	11,92	11,64	13,67	13,96	10,03
Water content of flue gas (related to fuel gas quantity)	H <sub>2</sub> O <sub>D</sub>	kg/m <sup>3</sup>	1,41	1,64	0,88	0,87	0,85	0,92
Dew point (dry combustion air)	t <sub>T</sub>	°C	58	58	58	54	53	62
<b>Composition</b>								
Nitrogen	N <sub>2</sub>	% Vol.	14,0	1,1	38,2	58,3	63,0	9,6
Oxygen	O <sub>2</sub>	% Vol.	—	—	7,8	15,5	16,8	0,5
Carbon dioxide	CO <sub>2</sub>	% Vol.	0,8	1,0	0,5	—	—	2,3
Hydrogen	H <sub>2</sub>	% Vol.	—	—	—	—	—	54,5
Carbon monoxide	CO	% Vol.	—	—	—	—	—	5,5
Methane	CH <sub>4</sub>	% Vol.	81,8	93,0	51,4	—	—	24,4
Ethane	C <sub>2</sub> H <sub>6</sub>	% Vol.	2,8	3,0	1,7	—	—	2,5
Propane	C <sub>3</sub> H <sub>8</sub>	% Vol.	0,4	1,3	0,3	24,9	—	0,7
Butane	C <sub>4</sub> H <sub>10</sub>	% Vol.	0,2	0,6	0,1	1,3	20,2	—
Total	Σ	% Vol.	100	100	100	100	100	100

1) Gas 62.8%, air 37.2%

2) Propane/Butane = 95/5; gas 26.2% / air 73.8%

3) Butane = 100%; gas 20.2% / air 79.8%

Fig.3.  
Composition and features of different gaseous fuels

Physical parameters of combustion.Heating value

Heating value (calorific value) is the heat released by the fuel when completely burnt, and may be determined at constant volume or constant pressure, and flue gas is cooled back to the initial temperature (ambient temperature).

- higher ( gross) heating value ( HHV ) - assumes that the water vapour in the products condenses and thus includes the latent heat of vapourisation of the water vapour in the products.
- lower heating value ( LHV ) - does not. contain the latent heat, the water in flue gas remain in steam form at the initial temperature

$$LHV = HHV - m_w \cdot h_{fg} - 9 \cdot m_{H_2} \cdot h_{fg}$$

$m_w$  = mass of water vapour per unit mass of fuel

$h_{fg}$  = latent heat of vaporization of water vapour / at its partial pressure in the combustion products [J/kg<sub>H2O</sub>]

$m_{H_2}$  = mass of original hydrogen per unit mass of fuel.

Combustion is a process that starts from a nonequilibrium condition, but equilibrium may not be achieved in a flame, that depends on the kinetics. A quasi equilibrium, is achieved, approximately in such cases, if combustion process are fast relative to the rate of heat loss by convection, radiation, one can collocate the maximum temperature of combustion products.

This is the adiabatic flame temperature in the case of burning gaseous fuel under stoichiometric condition

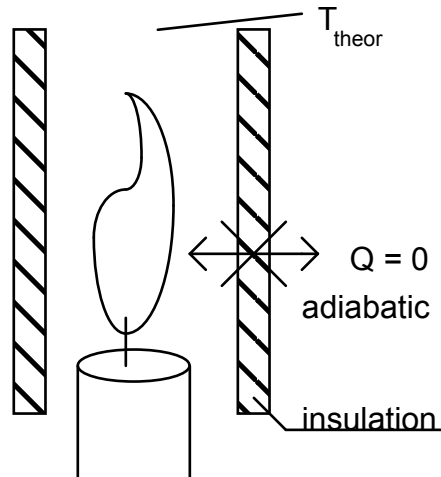
$$\begin{aligned} 1. \quad q_{gas} &= \bar{c}_{pg} \cdot (T_g - 273) \quad \left[ \frac{kJ}{m^3_{gas}} \right] \\ 2. \quad q_{air} &= \bar{c}_{pair} \cdot (T_{air} - 273) \cdot L'_0 \quad \left[ \frac{kJ}{m^3_{air}} \right] \\ 3. \quad q_{fuel} &= H_u \quad \left[ \frac{kJ}{m^3_{fuel}} \right] \end{aligned}$$

All of these are increasing the enthalpy of the flue (burnt) gas.

$$4. \quad q_{fg} = \bar{c}_{pfg} \cdot (T_{theor} - 273) \cdot V'_0 \quad \left[ \frac{kJ}{m^3_{fluegas}} \right]$$

$$q_{gas} = q_{gas} + q_{air} + q_{fuel}$$

$$T_{theor} = 273 + \frac{q_{gas} + q_{air} + q_{fuel}}{V'_0 \cdot \bar{c}_{pfg}}$$

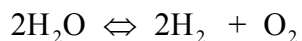
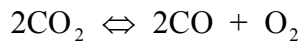


### Remarks

For hot flames -roughly for flames hotter than 2000°K assuming simple burning to CO<sub>2</sub> and H<sub>2</sub>O leads to significant errors. It is the dissociation of gases, which process need heat, so the flame temperature will be lower from the theoretical one.

The difference is at 2000 °C less than 7 % ( at 1500 °C 0 %)

Reactions of dissociation:



Both of these reactions can take place simultaneously in the same combustion process, and the necessary heat for the reaction comes from the flame.

These type of reactions are called endothermic reactions.

To start the chemical reactions it is necessary to supply to the species the activation energy.

Arrhenius stated that really those molecules which possess energy greater than a certain amount  $E_A$  will react. These high energy active molecules lead to products.

Arrhenius postulate may be written as

$$k = k_0 \cdot e^{-\frac{E_A}{R \cdot T}}$$

The temperature dependence of "k" is expressed in this equation.

And the rate of reaction is

$$w = \frac{dc}{dt} = k \cdot c$$

where **c** is used to denote the concentration in a chemical reacting system.]

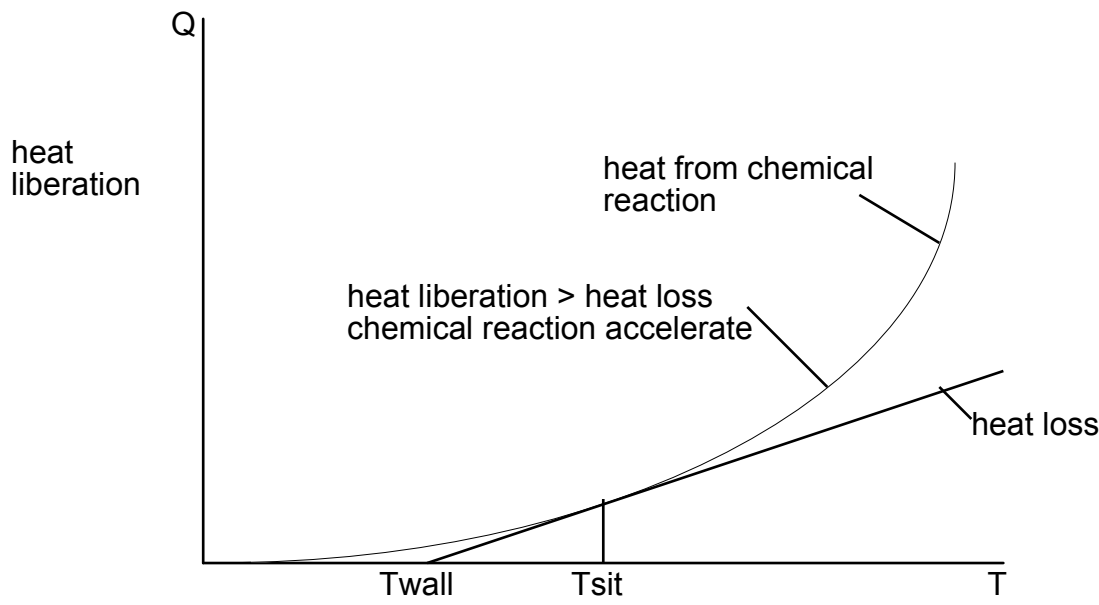
The activation energy can be added to the mixture by spark, or by other heat source..

### Spontaneous ignition temperature

When a gaseous mixture of fuel and oxidant is maintained at ambient temperature, reaction rates are extremely slow.

Increasing the mixture temperature, the reaction rate suddenly increases, giving rise to rapid combustion reactions

This condition is referred to as spontaneous ignition and the minimum temperature at which rapid combustion reactions are initiated is called the spontaneous ignition temperature.  $[T_{sit}]$   
The factors influencing the spontaneous ignition temperature of a given mixture are the balance between heat release and heat loss, as well as the supply of reactants.



For liquid fuels, this parameter is determined using standardized tests, where liquid fuel is dropped into an open-air container heated to a known temperature.

The spontaneous ignition temperature is defined as the lowest temperature at which visible or audible evidence of combustion is observed.

Minimum ignition energy

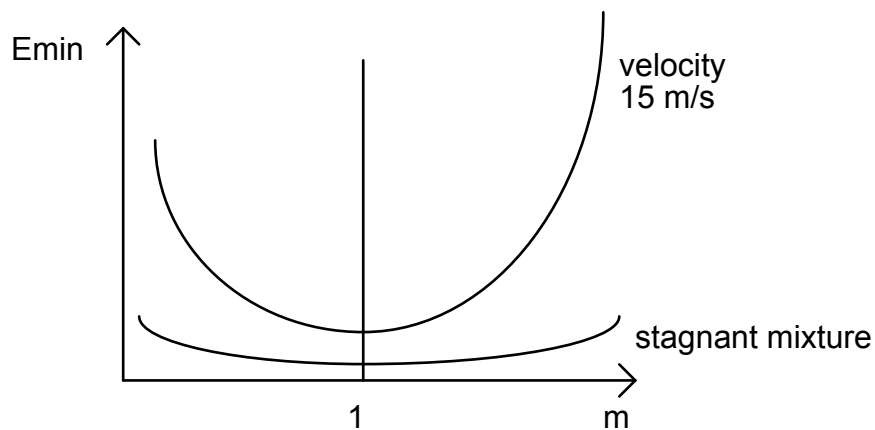
Minimum ignition energy is calculated on the assumption that sufficient energy must be supplied from exterior to the critical volume to raise the mixture temperature to the flame temperature  $T_f$ . The critical energy is thus

$$E = V_c \cdot \rho \cdot C_p \cdot (T_f - T_i)$$

where:  $\rho$  - density  
 $C_p$  - specific heat  
 $T_f$  - flame temperature  
 $T_i$  - initial temperature

The theoretical minimum ignition energy is calculated on the assumption that the energy is released from the ignition source instantaneously and homogeneously throughout the critical volume.

If the time duration of ignition is too long--> the energy will be transferred by thermal conductivity to the outside. In the critical volume the ignition cannot be achieved when the energy within the critical volume is insufficient to raise the mixture temperature to the flame temperature. For minimum ignition energies of the order of several millijoule of the energy must be released in several microseconds in order to ensure that there is no significant transfer of energy away from the ignition source.



Influence of velocity variation on minimum ignition energy

### Combustion equations - stoichiometric calculation

To do this calculations is needed to know the result of ultimate analysis of the fuel.

According to the basic elements of the fuel, we can write the combustion equations.

These are chemical equations which show:

- the reactants and the products of combustion
- the relative quantities of the reactants and products

These equations show only the beginning and the end of processes, and don't inform us about burning processes. But it is important to know how much air (or oxidiser) is needed, how much flue gas generate the process and which is the composition of the flue gas.

The detailed calculation shows the manual of the problem solving lesson.

### Excess air factor ( $\lambda$ ) or (m)

A stoichiometric mixture of air and fuel is one that contains just sufficient oxygen for the complete combustion of the fuel. A mixture which has an excess of air is termed a weak mixture, and one which has a deficiency of air is termed a rich mixture.

The excess air factor:

$$\lambda = \frac{\text{Air actually use}}{\text{Air stoichiometrically necessary}} = \frac{A}{A_0}$$

Optimum value of the excess air factor depend on fuel type and burner construction.

Some usual values of the excess air factor:

fuel	$\lambda$
gas	1.03 - 1.06
oil	1.09 - 1.15
coal	1.3 - 1.5

Reaction types of burning processes

There are two types of burning process reaction, which are homogenous and heterogenous reaction.

- homogenous reaction - when the fuel and the oxidiser (air) are in the same (gas) state
- heterogenous reaction - when the fuel and the oxidiser (air) are in different state

In case of gas fuel reactions are homogenous, because the fuel and air both are in gas state.

In case of liquid fuel also only homogenous reactions take place, because the fuel in liquid state can't burn, it can burn only in evaporated (gas) state.

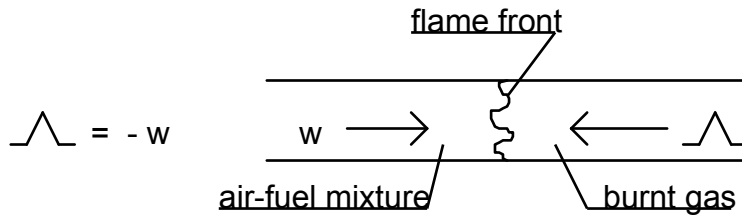
That's why we have to atomize liquid fuels for burning.

In case of solid fuel both, homogenous and heterogenous reaction take place.

Volatile matter burns in homogenous reaction, and the fix carbon (combustible solid) burns in heterogenous reaction.

Burning velocity

- velocity at which a flame propagates normally into unburned gas.



The leading edge of the propagating reaction zone is called flame front.

Burning velocity under kinetic control.

What does it mean?

There are two type of flames according to the nature of premixing of the reactants.

1, premixed flame

the reactants are completely mixed to the molecular level.

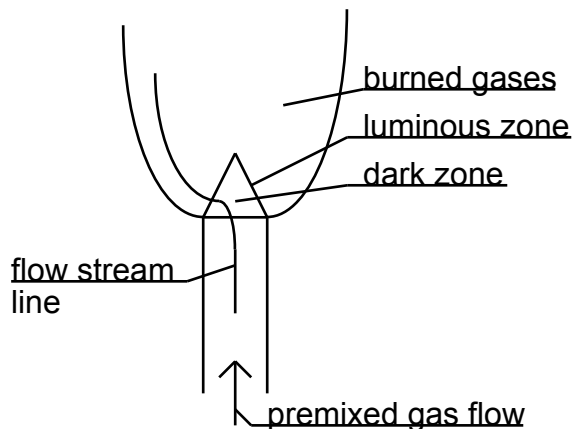
2, diffusion flame

propagating is controlled by the velocity at which the reactants diffuse toward each other.

Within these general divisions, there are imperfectly premixed flames, in which mixing may only be at the macro level but not completed at molecular level.

Completely premixed flames are seldom used in practice.

The Bunsen burner, domestic cooker are examples for more or less partially premixed flames. Premixed flames are kinetically controlled, and the rate of flame propagation, known as the burning velocity is dependent upon the chemical composition and rates of chemical reaction.



Characteristic of Bunsen burner flame

### Flame types

Flames are sorted according to two features, which are - mixing type of fuel and air  
- type of stream

Mixing types are:

- premixed flame - It means that fuel and air are mixed before ignition.
- diffusion flame - It means that fuel and air flow into burning chamber separately, and they are mixing there by means of diffusion.

Types of stream are:

- laminar flame
- turbulent flame (according to the Reynolds number of the flow)

A typical premixed laminar flame produced by Bunsen burner.

A typical turbulent premixed flame is produced by oxy-acetylene welding.

A typical laminar diffusion flame is produced by candle.

Turbulent diffusion flames generally produced by industrial burners.

### Parameters influencing the burning velocity

1, Fuel type	burning velocity
H <sub>2</sub>	280 cm/s
CH <sub>4</sub>	40 cm/s
CO	15 cm/s

It can be seen, that the hydrogen content of the fuel influences significantly the burning velocity.

### 2.Oxydizer

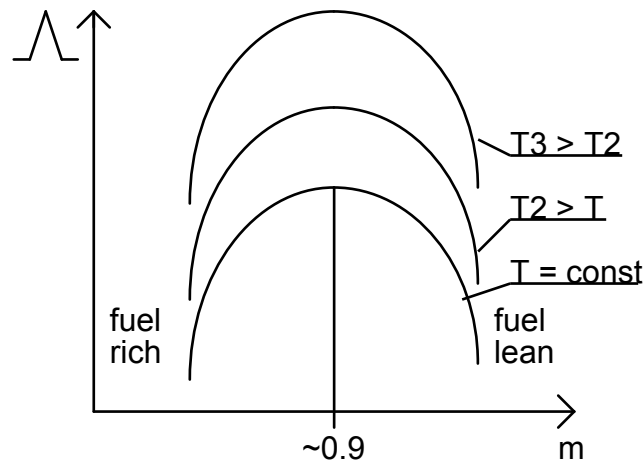
Instead of air using oxygen, the burning velocity increases (10x) tenfold. It's reason is that the oxidizer doesn't count N<sub>2</sub>, so the collision with oxygen is easier.

But the burning velocity decreases in air atmosphere polluted with exhaust gas, for example in a combustor of a gas turbine's afterburners.

### 3. Excess air factor

Flame can propagate through gaseous mixtures only within certain limits of composition. Limits of flammability can be determined experimentally by simply enclosing a mixture in a reactor and igniting the mixture by spark. The flame will propagate throughout the reactor, only within the upper and lower limits of mixture ratio.

A good definition for flammability limits is composition limits outside which the mixture will not permit the flame to propagate indefinitely, however powerful the source of ignition that is applied.



( $m = 1$  stoichiometric composition)

Combustion can occur only within the flammability limits. At the flammability limits the chemical reaction energy became less than the heat loss rate.

### 4. Influence of mixture temperature

Increasing the initial mixture temperature, the burning velocities increases.

### 5. Type of flow

Two main types of flow can occur:

- laminar
- turbulent

In laminar flames the burning velocity is less than in turbulent flames.

In turbulence case the heat and mass transport processes increases the velocity.

Parameter is the **Re** number.

### 6. Influence of pressure

The most combustion processes take place at atmospheric pressure but the burning velocity varies with pressure

$$\Lambda \sim p^n$$

$$\text{where } n \Rightarrow -0.3 \div 0.3$$

negative values are valid for small burning velocities ( $< 80 \text{ cm/s}$ )

positive values " " " higher " " ( $> 100 \text{ cm/s}$ )

### Quenching

The presence of walls in a combustion system generally results in heat losses from the flame and hot gases to walls which are usually at lower temperatures than the gases.

(Solid surfaces provide a means for breaking the chain propagation.)

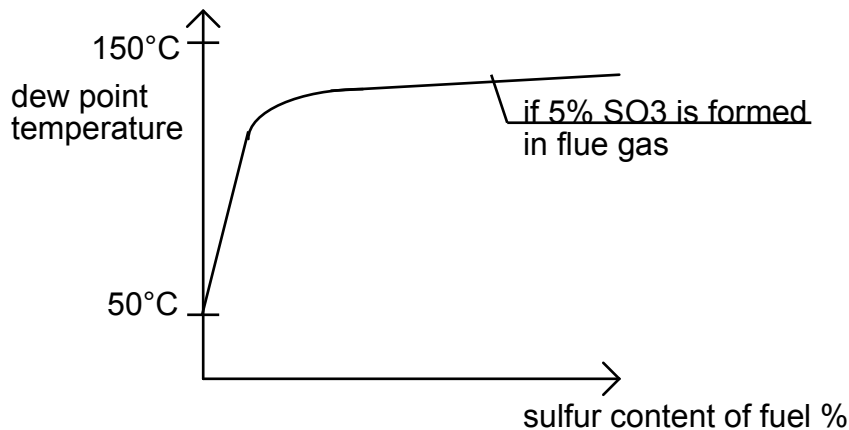
Generally the quenching diameter can be determined in the following manner. A flame is established on a burner port and the gas mixture flow is suddenly stopped. If the flame propagates down the tube, a smaller tube is substituted until propagation stops. The diameter of the tube which prevents flashback is the quenching distance or diameter.

Using a grid with a mesh distance less than the quenching distance, the flame cannot propagate through the grid. Such a solution is useful as a flame pitfall preventing flame propagation back in the supply tube.

Quenching distance is: 0,7 mm for hydrogen  
2,0 mm for methane  
1,8 mm for propane

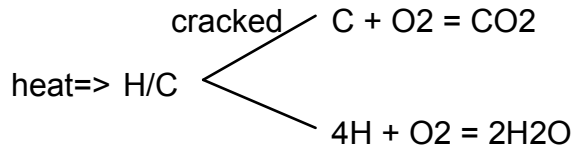
### Dew point

At low temperatures the dew point of fuel gas is reached and a liquid film of sulfuric acid forms on the metal surfaces of the air heater, greatly hastening metal failure.



### Cracking process

Different types of hydrocarbons are cracked at first and not directly oxidized.



Cracking breaks the H/C into carbon and hydrogen, which burn to carbondioxide and water. The incandescent ( lighting if heated ) carbon gives a yellow flame, and this type of flames (generally the diffusion flames ) are forming soot and smoke.

The solid carbon particles formed in flames, are known as soot. Soot can be formed from purely gaseous fuel, but is more commonly formed when liquid fuels are used, but also only after evaporating in the gas phase.

The presence of solid carbon plays an important role in the luminosity of flames and for flame, that rely on radiative heat transfer, the formation of soot particles is promoted. In automobile engines and other systems with watercooled surfaces, coking, due to the deposition of hard carbon deposits, can readily arise when fuel is allowed to come into direct contact with the cooled surface. The formation of soot particles in flames is due to the thermal decomposition of the hydrocarbons.

In gas turbine combustion chambers formation of solid particles is not promoted so as to minimize radiative heat transfer from the flame to the combustor-can wall and reduce the requirement for additional air cooling. Particles cause damage to gas turbine blades, deposit on it.

In industrial furnaces, flames are separated into two main regions:

- 1, luminous region, where particles are present
- 2, less luminous region, further downstream, where sufficient oxygen is supplied to allow reaction to be completed before the products leave the

combustion chamber.

Summarized:

- if the furnace is small and cold areas ( boiler tubes and the line ) are badly located carbon cannot possibly burn to completion.

### Soot formation

Soot is elementary carbon which derives from gas phase, as the result of burning gases decay. Soot wasn't in the burning gas.

Chemical bond between carbon atoms is stronger than between carbon and hydrogen atom, that is why hydrogen atoms burn to water first and then the carbon atoms to  $\text{CO}_2$ .

Pure carbone molecules in the flue gas are called soot.

Small amount of soot in the flame is advantageous, because it increase radiation of the flame.

Bigger radiation increase the heat-exchange from flue gas to water or steam.

But when the reaction is freezing before soot can burn to  $\text{CO}_2$ , it reamains in the flue gas, which's disadvantages (cause pollution).

### Coke formation

Mainly fuel oil has different forms of aromatic chain compounds.

Aromatic rings with free valence can link together. This cause the increasing of C/H ratio.

Above a certain level of C/H ratio this appears in solid form which is called coke.

These coke is disadvantages, because it makes a layer on heating surfaces and reduces heat transfer.

### Stability of flames

Investigating the flame stability means searching stability limits where the flame flashes back or blows off.

The essence of the matter that the ignition originate always from the burner mouth.

We use by this investigation the "speed limit gradient"

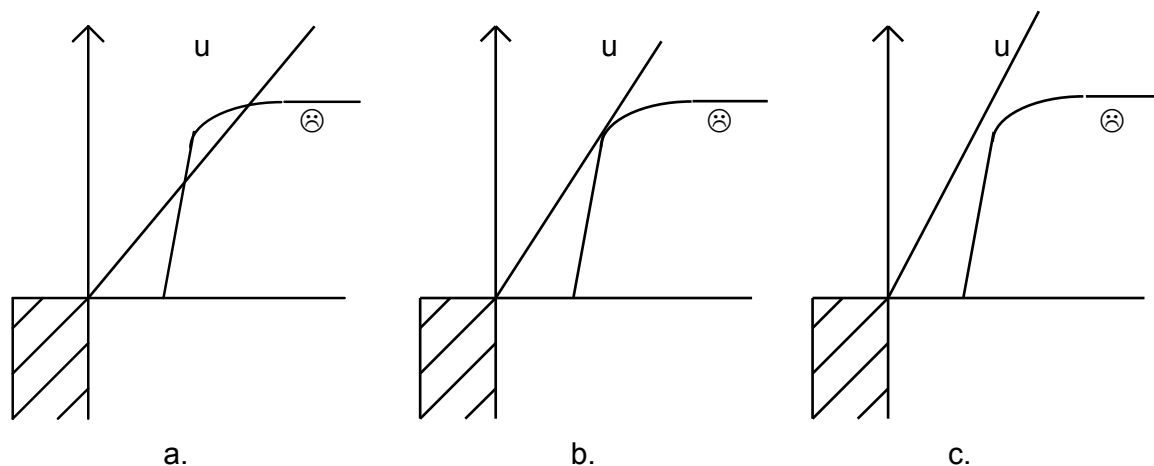
$$g = \frac{4 \cdot u_k}{r}$$

where  $u_k$  is the average speed  
in the burner mouth

Investigation of the flame stability spread over distribution of velocity along the wall of the burner mouth. In this boundary layer the distribution of velocity is linear that's why we can use the initial tangent of the parabolic distribution of velocity.

We are investigating what is the relation of the flow velocity and the burning velocity in the boundary layer.

The picture shows the three possible cases:

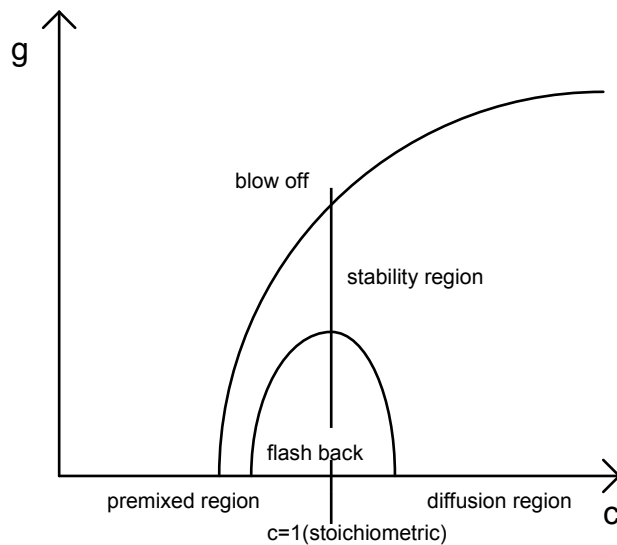


In case of "a" there are flash back, because there are some point of the line where burning velocity is bigger than flow velocity.

In case of "b" shows a stabile flame because at the tangent point burning velocity is equal with flow velocity.

In case of "c" there are blow off because the flow velocity is bigger everywhere than the burning velocity.

According to "Lewis & Elbe" we can show "g"(speed limit gradient) in a diagram against "c" (concentration).



### Flame stabilization

For burning stabilization are generally used inner and outer recirculation.

Inner recirculation can be reached by two means, mechanically and aerodynamically.

When we put a bluff body in front of the burner mouth, into the flame, behind the bluff body inner recirculation will take place.

we can reach inner recirculation using blades in burner mouth which cause recirculation aerodynamically.

The other stabilization method is the outer recirculation. It only in burning chamber takes place. (by free jet flames can't be)

Every types of recirculation deliver hot flue gas back to the burner mouth for helping the ignition.

## STOICHIOMETRIC CALCULATIONS

Stoichiometric calculations are needed because in that way can determine features of flue gas, which can be various at different fuels, and firing methods. Results of this calculations are needed for further calculations or decisions.

### 1. Input data

In case of solid or liquid fuels input data are the result of ultimate analysis by mass.

Input data:	C (Carbon)	[kg/kg fuel]
	H (Hydrogen)	[kg/kg fuel]
	S (Sulfur)	[kg/kg fuel]
	O (Oxygen)	[kg/kg fuel]
	N (Nitrogen)	[kg/kg fuel]
	w (Water)	[kg/kg fuel]
	a (Ash)	[kg/kg fuel]
<hr/>		1.00

In case of gaseous fuels input data are the result of molecule analysis by volume.

Input data:	CH <sub>4</sub> (Methane)	[m <sup>3</sup> /m <sup>3</sup> fuel]
	C <sub>2</sub> H <sub>6</sub> (Ethane)	[m <sup>3</sup> /m <sup>3</sup> fuel]
	C <sub>3</sub> H <sub>8</sub> (Propane)	[m <sup>3</sup> /m <sup>3</sup> fuel]
	C <sub>4</sub> H <sub>10</sub> (Butane)	[m <sup>3</sup> /m <sup>3</sup> fuel]
	C <sub>m</sub> H <sub>n</sub> (further hydro-carbon components)	[m <sup>3</sup> /m <sup>3</sup> fuel]
	CO (Carbon monoxide)	[m <sup>3</sup> /m <sup>3</sup> fuel]
	H <sub>2</sub> (Hydrogen)	[m <sup>3</sup> /m <sup>3</sup> fuel]
	CO <sub>2</sub> (Carbon dioxide)	[m <sup>3</sup> /m <sup>3</sup> fuel]
	N <sub>2</sub> (Nitrogen)	[m <sup>3</sup> /m <sup>3</sup> fuel]
	O <sub>2</sub> (Oxygen)	[m <sup>3</sup> /m <sup>3</sup> fuel]
	H <sub>2</sub> S (Hydrogen sulfide)	[m <sup>3</sup> /m <sup>3</sup> fuel]
	H <sub>2</sub> O (water vapor)	[m <sup>3</sup> /m <sup>3</sup> fuel]
<hr/>		1.00

Furthermore humidity content of air can be taken into account:  $x$  [kg water / kg air]

Value of excess air factor ( $\lambda$  - depends on firing method) is necessary for the calculation too.

## 2. Determination of specific quantities in case of solid or liquid fuels

Specific quantity means that it gives the quantity of different materials which are needed for burning, or produced by burning, in case of a unit (mass, or volume) fuel firing.

The calculation gives the result in mass unit and in volume unit as well.

For further calculations generally mass unit is used.

But flue gas analyzers generally give the result in volume composition.

The calculation at first step is valid for perfect combustion and without excess air ( $\lambda=1$ ).

Excess air will be taken into account in second step.

Products of imperfect combustion at normal operation take very small part in flue gas (less than 0.1 %), that is why these components do not make affect to the flue gas behaviour.

Calculations based on chemical equations, and on molar- or mass-ratios given by these equations. (See detailed in problem solving section.)

Specific quantities are the following:

(volume units are related to "normal state",  $p = 1 \text{ bar}$ ,  $t = 0 \text{ }^{\circ}\text{C}$ )

Oxygen and air demand:

Specific oxygen demand:	$\mu_{\text{O}_2}$	[kg/kg fuel]
	$\text{O}_2'$	[m <sup>3</sup> /kg fuel]
Specific air demand:	$\mu_{\text{L}_0}'$	[kg/kg fuel]
	$\text{L}_0'$	[m <sup>3</sup> /kg fuel]

Flue gas composition:

Specific carbon dioxide quantity:	$\mu_{\text{CO}_2}$	[kg/kg fuel]
	$\text{V}_{\text{CO}_2}$	[m <sup>3</sup> /kg fuel]
Specific sulfur dioxide quantity:	$\mu_{\text{SO}_2}$	[kg/kg fuel]
	$\text{V}_{\text{SO}_2}$	[m <sup>3</sup> /kg fuel]
Specific nitrogene quantity:	$\mu_{\text{N}_2}$	[kg/kg fuel]
	$\text{V}_{\text{N}_2}$	[m <sup>3</sup> /kg fuel]
Specific water vapor quantity:	$\mu_{\text{H}_2\text{O}}$	[kg/kg fuel]
	$\text{V}_{\text{H}_2\text{O}}$	[m <sup>3</sup> /kg fuel]

Calculation of these quantities flows according to the following.

The input data vector (results of ultimate analysis) has to be scalar multiplied with the appropriate constant vector from the following tables.

Constant vectors for specific quantities by mass:

	$\mu_{O_2}$	$\mu_{L_0}'$	$\mu_{CO_2}$	$\mu_{SO_2}$	$\mu_{N_2}$	$\mu_{H_2O}$
C	2.664	11.484	3.664	0	8.820	0
H	7.936	34.209	0	0	26.273	8.936
S	0.998	4.301	0	1.998	3.303	0
O	- 1.000	- 4.301	0	0	- 3.310	0
N	0	0	0	0	1.000	0
w	0	0	0	0	0	1.000
a	0	0	0	0	0	0

Constant vectors for specific quantities by volume:

	$O_2'$	$L_0'$	$V_{CO_2}$	$V_{SO_2}$	$V_{N_2}$	$V_{H_2O}$
C	1.864	8.876	1.8535	0	7.012	0
H	5.560	26.476	0	0	20.916	11.120
S	0.698	3.324	0	0.683	2.635	0
O	- 0.700	- 3.322	0	0	- 2.622	0
N	0	0	0	0	0.800	0
w	0	0	0	0	0	1.240
a	0	0	0	0	0	

Considering humidity of air:

$$\mu_{L_0'h} = \mu_{L_0}' \cdot (1 + x) \quad [\text{kg/kg fuel}]$$

$$\mu_{H_2O'h} = \mu_{H_2O}' + x \cdot \mu_{L_0}' \quad [\text{kg/kg fuel}]$$

Specific flue gas quantities:

Specific dry flue gas quantity:  $\mu_{V_o'd} = \mu_{CO_2} + \mu_{SO_2} + \mu_{N_2} \quad [\text{kg/kg fuel}]$

$$V_{o'd}' = V_{CO_2} + V_{SO_2} + V_{N_2} \quad [\text{m}^3/\text{kg fuel}]$$

Specific wet flue gas quantity:  $\mu_{V_o'} = \mu_{V_o'd} + \mu_{H_2O'h} \quad [\text{kg/kg fuel}]$

$$V_{o'}' = V_{o'd}' + V_{H_2O} \quad [\text{m}^3/\text{kg fuel}]$$

Calculation of lower heating value:

(It gives only approximate result, because of the different molecule composition of different fuels.)

$$H_i = 338.22 + 1195.9 \cdot (H - O/8) + 92.51 \cdot S - 25.1 \cdot w \quad [\text{kJ/kg}]$$

### 3. Determination of specific quantities in case of gaseous fuel

Input data are the result of molecule analysis by volume.

For mass quantity calculation first has to be determined the composition by mass.

It can be done for example in case of methane:

$$m_{CH_4} = \frac{V_{CH_4} \cdot \rho_{CH_4}}{\rho_{gas}} \quad [\text{kg/kg gas}]$$

where density of gaseous fuel can be determined according to the following.

The input data vector (results of molecular analysis by volume) has to be scalar multiplied with the constant vector of density vector belonging to each component.

$$\rho_{gas} = \sum V_i \cdot \rho_i \quad [\text{kg/m}^3]$$

Specific quantities are the following:

(volume units are related to "normal state",  $p = 1 \text{ bar}$ ,  $t = 0 \text{ }^\circ\text{C}$ )

Oxygen and air demand:

Specific oxygen demand:	$\mu_{O_2}$	[kg/kg fuel]
	$O_2'$	[m <sup>3</sup> /m <sup>3</sup> fuel]
Specific air demand:	$\mu_{L_0}'$	[kg/kg fuel]
	$L_0'$	[m <sup>3</sup> /m <sup>3</sup> fuel]

Flue gas composition:

Specific carbon dioxide quantity:	$\mu_{CO_2}$	[kg/kg fuel]
	$V_{CO_2}$	[m <sup>3</sup> /m <sup>3</sup> fuel]
Specific sulfur dioxide quantity:	$\mu_{SO_2}$	[kg/kg fuel]
	$V_{SO_2}$	[m <sup>3</sup> /m <sup>3</sup> fuel]
Specific nitrogen quantity:	$\mu_{N_2}$	[kg/kg fuel]
	$V_{N_2}$	[m <sup>3</sup> /m <sup>3</sup> fuel]
Specific water vapor quantity:	$\mu_{H_2O}$	[kg/kg fuel]
	$V_{H_2O}$	[m <sup>3</sup> /m <sup>3</sup> fuel]
Heating value of gas:	$H_i$	[kJ/kg fuel]
	$H_{Vi}$	[kJ/m <sup>3</sup> fuel]

Calculation of these quantities flows according to the following. Both input data vector has to scalar multiply with the appropriate constant vector from the following tables.

Constant vectors for specific quantities by mass:

	$\rho_{\text{gas}}$	$\mu_{\text{O}_2}$	$\mu_{\text{L}_0'}$	$\mu_{\text{CO}_2}$	$\mu_{\text{SO}_2}$	$\mu_{\text{N}_2}$	$\mu_{\text{H}_2\text{O}}$	$H_i$
$m_{\text{CH}_4}$	0.716	3.990	17.196	2.743	0	13.207	1.246	50103
$m_{\text{C}_2\text{H}_6}$	1.342	3.725	16.056	2.927	0	12.331	1.798	48005
$m_{\text{C}_3\text{H}_8}$	1.967	3.628	15.640	2.994	0	12.012	1.634	47222
$m_{\text{C}_4\text{H}_{10}}$	2.593	3.579	15.426	3.029	0	11.847	1.550	47687
$m_{\text{C}_n\text{H}_m}$	2.503	3.423	14.751	3.183	0	11.328	1.285	46174
$m_{\text{CO}}$	1.25	0.571	2.461	1.571	0	1.890	0	10098
$m_{\text{H}_2}$	0.09	7.937	34.206	0	0	26.271	8.935	119766
$m_{\text{CO}_2}$	1.977	0	0	1.000	0	0	0	0
$m_{\text{N}_2}$	1.251	0	0	0	0	1.000	0	0
$m_{\text{O}_2}$	1.428	- 1.000	- 4.310	0	0	- 3.310	0	0
$m_{\text{H}_2\text{S}}$	1.5384	1.409	6.071	0	1.880	4.662	0	386
$m_{\text{H}_2\text{O}}$	0.804	0	0	0	0	0	1.000	0

Constant vectors for specific quantities by volume:

	$\text{O}_2'$	$\text{L}_0'$	$V_{\text{CO}_2}$	$V_{\text{SO}_2}$	$V_{\text{N}_2}$	$V_{\text{H}_2\text{O}}$	$H_{V_i}$
$V_{\text{CH}_4}$	2.0	9.524	1.0	0	7.524	2.0	35874
$V_{\text{C}_2\text{H}_6}$	3.5	16.666	2.0	0	13.166	3.0	64423
$V_{\text{C}_3\text{H}_8}$	5.0	23.810	3.0	0	18.810	4.0	92887
$V_{\text{C}_4\text{H}_{10}}$	6.5	30.952	4.0	0	24.452	5.0	123654
$V_{\text{C}_n\text{H}_m}$	6.0	28.571	4.0	0	22.571	4.0	115575
$V_{\text{CO}}$	0.5	2.381	1.0	0	1.881	0	12623
$V_{\text{H}_2}$	0.5	2.381	0	0	1.881	1.0	10779
$V_{\text{CO}_2}$	0	0	1.0	0	0	0	0
$V_{\text{N}_2}$	0	0	0	0	1.000	0	0
$V_{\text{O}_2}$	- 1.0	- 4.762	0	0	- 3.762	0	0
$V_{\text{H}_2\text{S}}$	1.5	7.143	0	1.0	5.643	1.0	594
$V_{\text{H}_2\text{O}}$	0	0	0	0	0	0	0

Considering humidity of air:

$$\mu_{\text{L}_0'h} = \mu_{\text{L}_0'} \cdot (1 + x) \quad [\text{kg/kg fuel}]$$

$$\mu_{\text{H}_2\text{O}h} = \mu_{\text{H}_2\text{O}} + x \cdot \mu_{\text{L}_0'} \quad [\text{kg/kg fuel}]$$

Specific flue gas quantities:

Specific dry flue gas quantity:  $\mu_{V_o'd} = \mu_{\text{CO}_2} + \mu_{\text{SO}_2} + \mu_{\text{N}_2} \quad [\text{kg/kg fuel}]$   
 $V_{o'd}' = V_{\text{CO}_2} + V_{\text{SO}_2} + V_{\text{N}_2} \quad [\text{m}^3/\text{m}^3 \text{ fuel}]$

Specific wet flue gas quantity:  $\mu_{V_o'} = \mu_{V_o'd} + \mu_{\text{H}_2\text{O}h} \quad [\text{kg/kg fuel}]$   
 $V_{o'}' = V_{o'd}' + V_{\text{H}_2\text{O}} \quad [\text{m}^3/\text{m}^3 \text{ fuel}]$

#### 4. Determination of $RO_{2\max}$

Knowing  $RO_{2\max}$  value can help the evaluation of the results of flue gas analysis.

Determination: 
$$RO_{2\max} = \left( \frac{V_{CO_2}}{V_{O_2}} + \frac{V_{SO_2}}{V_{O_2}} \right) \cdot 100 \quad [\%]$$

At different fuel types this value:	coal:	18.3 - 19.5	%
	wood	20.0 - 21.0	%
	heavy oil:	15.9 - 16.1	%
	light oil:	15.4 - 15.6	%
	natural gas:	11.5 - 12.1	%
	city gas:	10.8 - 11.7	%

#### 5. Considering excess air

Generally firing happens with excess air, so as to reach the perfect combustion.

Calculation of real quantities are follows:

Inducted air:

$$\begin{aligned} \mu_{L'} &= \lambda \cdot \mu_{L_{O'}} & [\text{kg/kg fuel}] \\ L' &= \lambda \cdot L_{O'} & [\text{m}^3/\text{m}^3 \text{ or kg fuel}] \end{aligned}$$

Specific dry flue gas quantity:

$$\begin{aligned} \mu_{V'd} &= \mu_{V_{O'd}} + (\lambda - 1) \cdot \mu_{L_{O'}} + a \cdot (1 - s) & [\text{kg/kg fuel}] \\ V'd &= V_{O'd} + (\lambda - 1) \cdot L_{O'} & [\text{m}^3/\text{m}^3 \text{ or kg fuel}] \end{aligned}$$

Specific flue gas quantity:

$$\begin{aligned} \mu_{V'} &= \mu_{V_{O'}} + (\lambda - 1) \cdot \mu_{L_{O'}} + a \cdot (1 - s) & [\text{kg/kg fuel}] \\ V' &= V_{O'} + (\lambda - 1) \cdot L_{O'} & [\text{m}^3/\text{m}^3 \text{ or kg fuel}] \end{aligned}$$

where: s - shows the remaining part of ash in the fire chamber

Calculation the actual flue gas composition:

Specific carbon dioxide quantity:	$\mu_{rCO_2} = \mu_{CO_2} / \mu_{V'}$	[kg/kg flue gas]
	$V_{rCO_2} = V_{CO_2} / V'$	[m <sup>3</sup> /m <sup>3</sup> flue gas]
Specific sulfur dioxide quantity:	$\mu_{rSO_2} = \mu_{SO_2} / \mu_{V'}$	[kg/kg flue gas]
	$V_{rSO_2} = V_{SO_2} / V'$	[m <sup>3</sup> /m <sup>3</sup> flue gas]
Specific nitrogene quantity:	$\mu_{rN_2} = \mu_{N_2} / \mu_{V'}$	[kg/kg flue gas]
	$V_{rN_2} = V_{N_2} / V'$	[m <sup>3</sup> /m <sup>3</sup> flue gas]
Specific water vapor quantity:	$\mu_{rH_2O} = \mu_{H_2O} / \mu_{V'}$	[kg/kg flue gas]
	$V_{rH_2O} = V_{H_2O} / V'$	[m <sup>3</sup> /m <sup>3</sup> flue gas]
Specific air quantity:	$\mu_{rair} = (\lambda - 1) \cdot \mu_{Lo'} / \mu_{V'}$	[kg/kg flue gas]
	$V_{rair} = (\lambda - 1) \cdot L_o' / V'$	[m <sup>3</sup> /m <sup>3</sup> flue gas]
Specific flying ash quantity:	$\mu_{ra} = a \cdot (1 - s) / \mu_{V'}$	[kg/kg flue gas]
(only at solid fuels)	$V_{ra} = a \cdot (1 - s) / V'$	[kg/m <sup>3</sup> flue gas]

Excess air calculation from measured data:

From the equations:  $V'_{sz} = V_o'_{sz} + (\lambda - 1) \cdot L_o'$  , and

$$RO_{2max} \cdot V_o'_{sz} = RO_{2measured} \cdot V'_{sz}$$

can derived the following equation:  $\lambda = 1 + \left( \frac{RO_{2max}}{RO_{2measured}} - 1 \right) \cdot \frac{V_o'_{sz}}{L_o'}$

taking into consideration that  $V_o'_{sz} \approx L_o'$  can get:  $\lambda = \frac{RO_{2max}}{RO_{2measured}}$

Or from oxigen content:

From the equations:  $V'_{sz} = V_o'_{sz} + (\lambda - 1) \cdot L_o'$  , and

$$RO_{2max} \cdot V_o'_{sz} = RO_{2measured} \cdot V'_{sz}$$

$$0.21 \cdot (\lambda - 1) \cdot L_o' = O_{2measured} \cdot (V_o'_{sz} + (\lambda - 1) \cdot L_o')$$

taking into consideration that  $V_o'_{sz} \approx L_o'$  can get:  $\lambda = \frac{21}{21 - O_{2measured}}$

# ATOMIZATION<sup>1</sup>

## 1. Why does atomization play an important role in combustion of liquid fuels?

The processes of liquid atomization and evaporation are of fundamental importance to the behaviour of combustion system. Normal fuels are not sufficiently volatile to produce vapour in the amounts required for ignition and combustion unless they are *atomized* into a large number of drops with corresponding vastly increased surface area.

The smaller the drop size, the faster the rate of evaporation. The influence of drop size on *ignition* performance is of special importance, since large increase in ignition energy are needed to overcome even a slight deterioration in atomization quality. Spray quality also affects *stability*, *combustion efficiency*, and the *emission levels* of smoke, carbon monoxide, and unburned hydrocarbons.

An example on combustion efficiency can show the importance of atomization on combustion [1].

Combustion efficiency is defined as the ratio of the mass of fuel evaporated within the combustion zone to the mass of fuel supplied:

$$\eta_c = \frac{\dot{m}_F \cdot t_{\text{res}}}{\rho_g \cdot \frac{V_c}{\mu_{Lo}}}$$

where

- $\dot{m}_F$  : mass flow rate of fuel, [kg/s]
- $t_{\text{res}}$  : residence time of fuel in combustion zone, [sec]
- $\rho_g$  : gas density (air), [kg/m<sup>3</sup>]
- $V_c$  : volume of combustion zone, [m<sup>3</sup>]
- $\mu_{Lo}$  : air-fuel ratio by mass, [-]

Applying theory and practice in case when evaporation rate governs combustion the combustion efficiency is inversely proportional with the initial drop size as follows.

$$\eta_c \sim \frac{1}{\sqrt{D_o^3}}$$

It means that if we reduce the initial mean drop size by half we can increase the combustion efficiency up to  $\sqrt[3]{8} \cong 2.8$  times of its initial value.

---

<sup>1</sup> Ref.: ATOM1A.DOC + ATOM1B.DOC

**2. What does atomization mean and how does the final fuel spray look like (spray characteristics)?**

Atomization is the process whereby a volume of liquid is converted into a multiplicity of small drops. Its principal aim is to produce a high ratio of surface to mass in the liquid phase, resulting in very high evaporation rate.

For most liquids, all that is needed is the existence of a high *relative* velocity between the liquid to be atomized and the surrounding air or gas.

With some atomizers this is accomplished by discharging the liquid at high velocity into a relatively slow moving stream of air or gas.

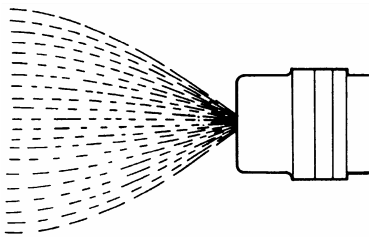


Fig. 1. Spray produced by swirl-pressure atomizer

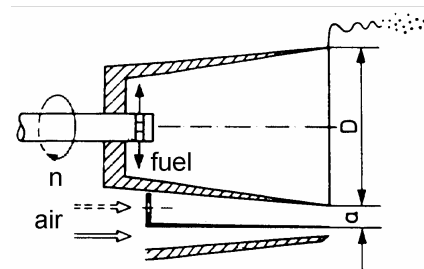


Fig. 2. Schematic layout of rotary cup atomizer

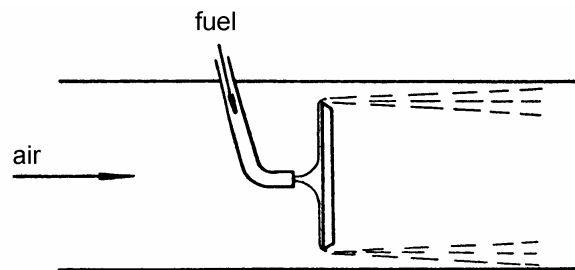


Fig. 3. Air blast atomization process

Notable examples include the various forms of *pressure atomizer* (Fig. 1.) and *rotary atomizers* (Fig. 2.), which eject the liquid at high velocity from the periphery of a rotating cup or disk.

An alternative approach is to expose the relatively slow-moving liquid to a high-velocity air-stream (Fig. 3.). This method is generally known as *twin-fluid*, *air-assist*, or *air blast* atomization.

## Spray characteristics

The important spray characteristics are:

### a. Drop Size Distribution

Only under certain special condition can a fairly homogeneous spray be produced (e.g. rotary cup atomizer operating within a limited range of fuel flow rates and rotational speeds). Thus the resulting main drops and satellite drops vary in size.

The drop sizes normally range in diameter 10 to 400  $\mu\text{m}$  depending on atomization characteristics and surrounding conditions.

Histogram, frequency distribution, and cumulative-distribution curve are used to represent the drop size distribution in sprays.

### Histogram of drop size

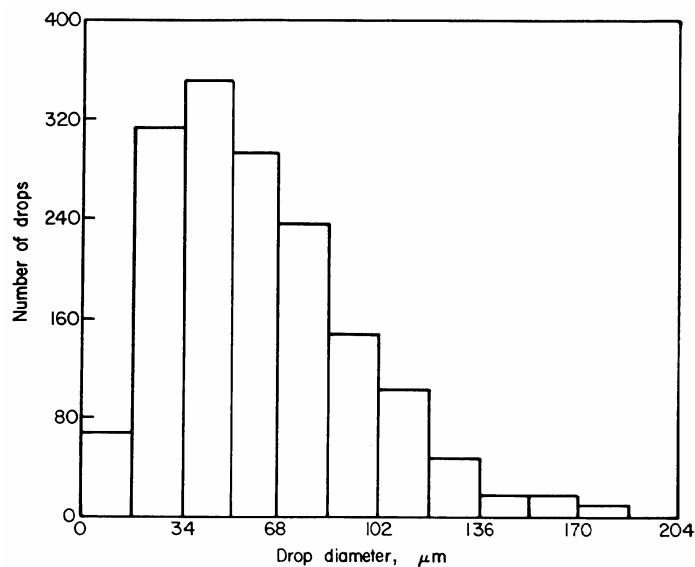


Fig. 4. Histogram of drop size shows the number of drops whose dimensions

$$\text{fall between the limits } x - \frac{\Delta x}{2} \text{ and } x + \frac{\Delta x}{2}$$

As  $\Delta x$  is made smaller, the histogram assumes the form of a *frequency curve* that may be regarded as a characteristic of the spray, provided it is based on sufficiently large samples.

### Frequency distribution curve

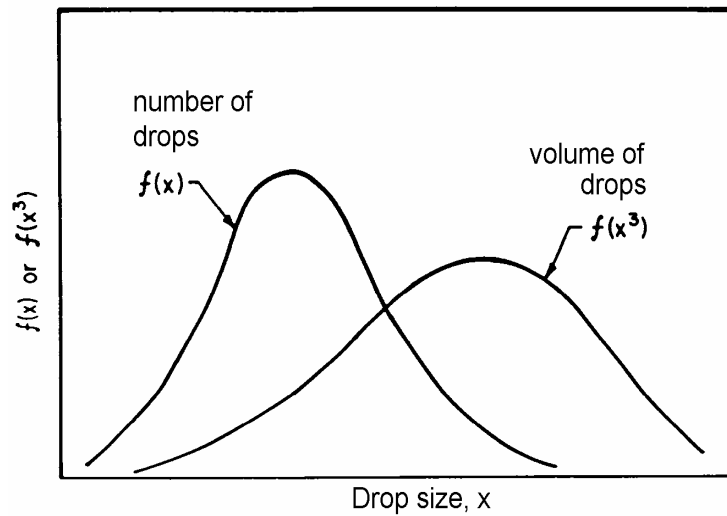


Fig. 5. Frequency distribution curve

### Cumulative-distribution curve

This is a plot of the integral of the frequency curve, and it may represent the percentage of the total number of drops in the spray below a given size, or it may express the percentage of the total surface or volume of spray contained in drops below a given size.

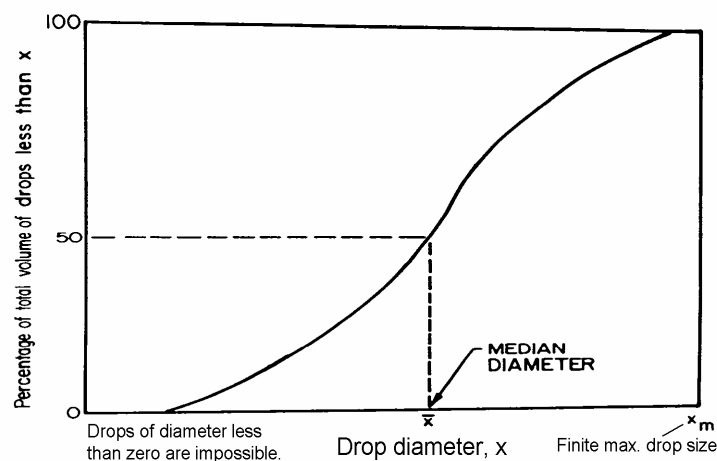


Fig. 6. Cumulative-distribution curve

### Expressions to replace experimental drop size distribution

Developed by Rosin and Rammler (1933)

$$1 - v = e^{(-b \cdot x)^q}$$

where

v: fraction of the total volume contained in drops of diameter less than x

b,q: constants representing the spray characteristics  
e.g. q shows the uniformity of the spray, the higher the value of q, the more uniform is the spray;  $q = \infty$  drops have the same size

For most fuel sprays the value of q lies between 2 and 4, however for air blast atomizer  $q \cong 2.59$  (measurement) and for rotary atomizer  $q = 7$ .

### b. Mean Drop Size

To facilitate the calculation of evaporation rates and to compare the atomization qualities of various sprays, the term *mean diameter* has been introduced.

The general idea being to replace a given spray with a fictitious one in which all the drops have the same diameter while retaining certain characteristics of the original spray.

#### Sauter Mean Diameter (SMD)

The most widely used SMD is the diameter of a drop having the same volume/surface ratio as the entire spray:

$$SMD = \frac{\sum_i n_i \cdot D_i^3}{\sum_i n_i \cdot D_i^2} \quad [m]$$

#### Mass Mean Diameter (MMD)

Diameter of drop below or above which lies 50 percent of the mass of the drops.

$$MMD = \left( \frac{\sum_i n_i \cdot D_i^3}{\sum_i n_i} \right)^{0.33}$$

**c. Penetration**

The penetration of a spray may be defined as the maximum distance it reaches when injected into *stagnant* air. It is governed by the relative magnitudes of two opposing forces:

- 1.) the kinetic energy of the initial fuel jet
- 2.) the aerodynamic resistance of the surrounding gas.

The initial jet velocity is high, but as atomization proceeds and the surface area of the spray increases, the kinetic energy of the fuel is gradually dissipated by frictional losses of the gas. When drops have finally exhausted their kinetic energy, their subsequent trajectory is dictated mainly by gravity and the movement of the surrounding gas.

In general, a compact, narrow spray (e.g. produced by Diesel injector) will have high penetration, while a well-atomized spray of high cone angle, including more air resistance, will tend to have low penetration.

Spray penetration is greater than that of a single drop due to the action of first droplets on the air in the spray.

**d. Paternation**

Paternation of a conical spray represents the uniformity of the circumferential distribution of fuel in it. Poor paternation adversely affects many important aspects of combustion performance by creating local pockets of mixture in the combustion zone that are either appreciably richer or weaker than the design fuel-air ratio.

**e. Cone Angle**

The spray angle has a strong influence on ignition, stability limits, and exhaust smoke.

e.g.: With pressure-swirl atomizer (described later, now see Fig. 1.) the hollow conical structure of the spray incurs appreciable exposure to the influence of the surrounding air. This leads to an improved atomization.

An increase in spray-cone angle (e.g. in case of higher load/mass flow rate of fuel) increases the extend of the above exposure resulting better atomization if other factors are not impair it.

### 3. What are the basic mechanisms of atomization process?

#### Diesel engine

Diesel engines employ a *plain-orifice atomizer* in which fuel is forced under pressure through a small hole and is discharged in the form of a jet that rapidly disintegrates into a well-atomized spray of narrow cone angle.

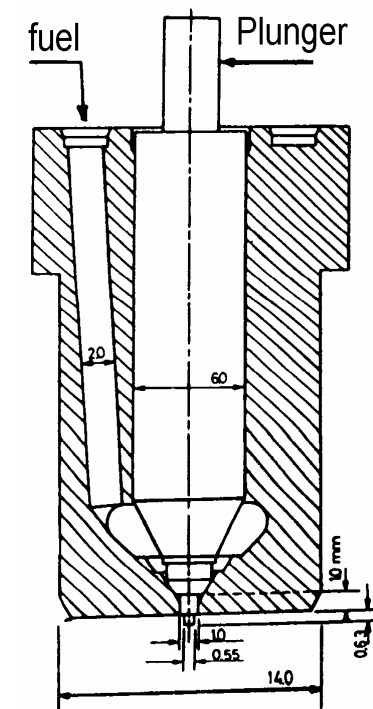


Fig. 7. Bosch pintle Diesel plain-orifice injector

#### Gas Turbine

In gas turbine atomization is normally accomplished by transforming the bulk fuel into fine jets or thin conical sheets in order to induce instability and promote disintegration into drops.

Thin sheets may be obtained by discharging the fuel through orifices with specially shaped approach passages, by forcing it through narrow slots, by feeding it to the centre of a rotating disc or cup.

Disintegration of the fuel jets or sheets into ligaments and then drops is induced by interaction with the surrounding air or gas (see Fig. 8.).

A certain difference exists between the velocity of the film and the ambient air or gas, when the liquid passes off either into the stagnant air or into the air stream. The existing small disturbances generate sine-shaped wave motion with increasing amplitude. The greater is the velocity difference, the shorter is the wave length ( $\lambda$ ) and the greater is the amplitude. The wave motion is caused by the depression, that is produced by the local higher air velocity, while over-pressure develops in the wave through.

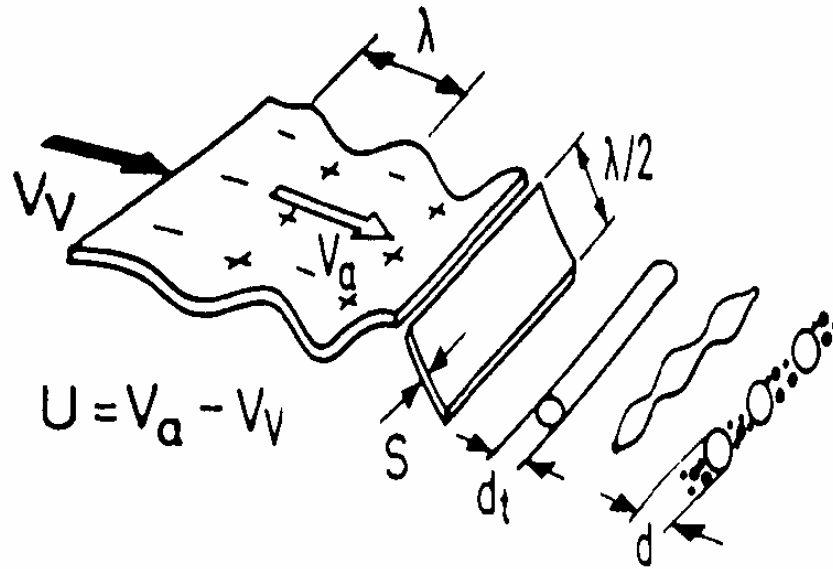


Fig. 8. Illustration of liquid break up into drops

The consequence of the increasing amplitude is that the film reaches the wave crest where a thin ligament is detached and further it breaks up into droplets.

An alternative method of atomization is to expose the fuel jets or sheets to a high-velocity air, which also serves to convey the resulting drops into the combustion zone.

#### Oil-fired furnaces

They use both pressure and air (or steam) atomization, and sometimes a combination of the two.

#### 4. Two dimensionless numbers indicating the quality and the nature of the atomization process.

The drop sizes obtained during liquid jet disintegration, due to the influence of the surrounding air, are governed by the ratio of the *disruptive aerodynamic force* ( $\rho_{air} \cdot U_{rel}^2$ ) to the *consolidating surface tension force* ( $\sigma/d_o$ ). This dimensionless ratio is known as the *Weber number*,

$$We = \frac{\rho_{air} \cdot U_{rel}^2}{\sigma/d_o}$$

where

$\rho_{air}$  : air density, [kg/m<sup>3</sup>]

$U_{rel}$  : air relative to liquid velocity, [m/s]

$\sigma$  : surface tension, [kg/s<sup>2</sup>]

$d_o$  : liquid orifice or initial jet diameter, [m]

The break-up mechanism of the jet is found to be dependent on the so-called "Z number", which is obtained as the ratio of the square root of the Weber number to the Reynolds number:

$$Z = \frac{We^{0.5}}{Re} = \left( \frac{\mu_L}{\sqrt{\sigma \cdot \rho_L \cdot d_o}} \right)$$

where

$\mu_L$  : dynamic viscosity of liquid, [kg/m sec]

$\rho_L$  : liquid density, [kg/m<sup>3</sup>]

For any given atomizer, where  $d_o$  and the relevant air and liquid properties are known, the relevant values of Weber and Z number provide a useful indication of both the quality and the nature of the atomization process.

For instance the higher the Weber number of an atomizer the bigger the deformation of drops due to the opposing disruptive and consolidating forces. At limit case the surface tension is equal with the dynamic pressure:

$$\frac{\sigma}{d_o} = \rho_{air} \cdot U_{rel}^2$$

Above the critical Weber number the drop break-up into two drops and the atomization quality is so increased. The critical Weber number depends on the Z number and on whether the air or gas moves or not.

- [1] Lefebvre, A. H.: "Fuel Atomization, Droplet Evaporation, and Spray Combustion" in Fossil Fuel Combustion, ed. by Bartok, W. and Sarofim A. F., Wiley 1991.

## 5. Different types of atomizers

### a. Pressure - Swirl Atomizers

*Operation:* Liquid fuel is introduced tangentially at high pressure into a swirl chamber and passes through a diffuser to a circular orifice exit. The liquid is attached to the walls of the diffuser and leaves the atomizer in the form of an annular film with a central air core, generated by the pressure differences within the mixing chamber.

If now we examine frictionless flow and apply the vortex law which say that,

$$r \cdot c_{\text{tang}} = \text{const.}$$

$r$  : radius

$c_{\text{tang}}$ : tangential velocity of liquid

the tangential velocity distribution at  $r = 0$  is found infinite.

This annular film spreads out to form a hollow conical spray, which becomes unstable and disintegrates into ligament and large drops and, finally, into spray.

Various types of simple swirl atomizers have been designed, they differ mainly in the method used to impart swirl to the issuing jet.

A major drawback of the simplex atomizer is that its flow rate varies as the square root of the injection pressure differential (see Fig. 11/a,b.):

$$m_{\text{fuel}} \sim \sqrt{\Delta p}$$

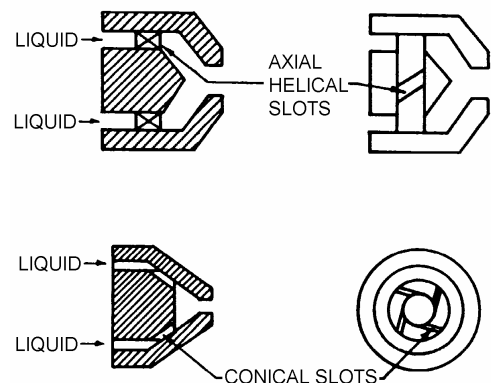
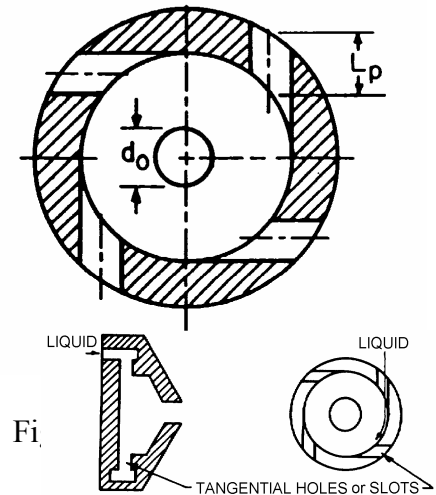
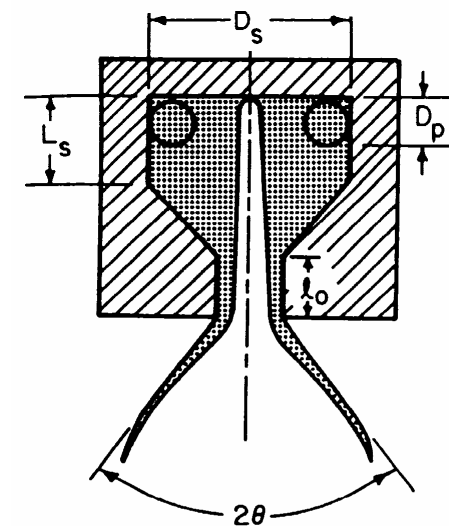


Fig. 10. Different types of simplex atomizers

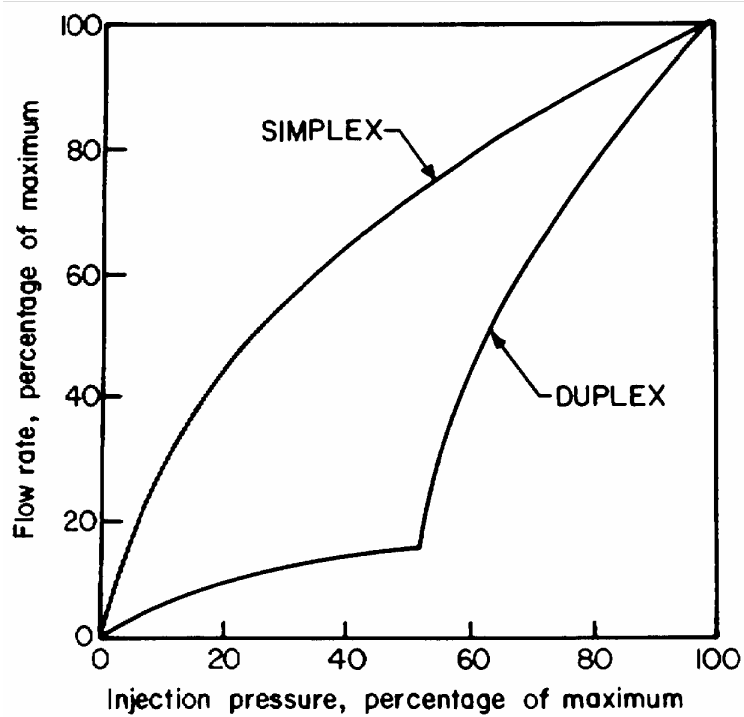


Fig. 11/a. Flow characteristics of simplex and duplex atomizers.

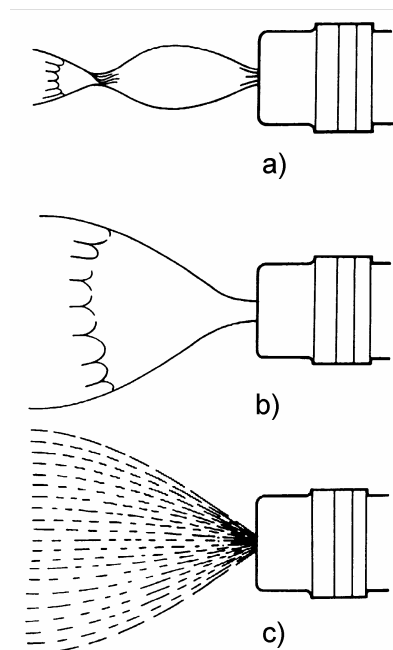


Fig. 11/b. Various stages of fuel atomization

- a) At low fuel pressures a continuous film of fuel is formed known as a 'bubble'
- b) At intermediate fuel pressures the film breaks up at the edges to form a 'tulip'
- c) At high fuel pressures the tulip shortens toward the orifice and forms a finely atomized spray

Thus doubling the flow rate demands a fourfold increase in fuel injection pressure. If the burner orifice is made small enough to ensure good atomization at a low fuel flow,

then the pressure required at high flows is excessive. On the other hand, if the orifice is made larger, the fuel will not atomize satisfactorily at the low flows.

This basic drawback of the simple atomizer has led to the development of various "wide-range" atomizers such as *duplex*, *dual-orifice*, and *spill-return* atomizers (see Fig. 12.).

The principal advantage of pressure-swirl atomizers are good mechanical reliability and an ability to sustain combustion at very weak mixture strengths.

Their drawback include potential *plugging* of the small passages and orifices by contaminants in the fuel and an innate tendency toward high soot formation at high combustion pressure (gas turbine application) when the injected fuel is only able to penetrate a short distance from the atomizer and thus a fuel-rich region is created.

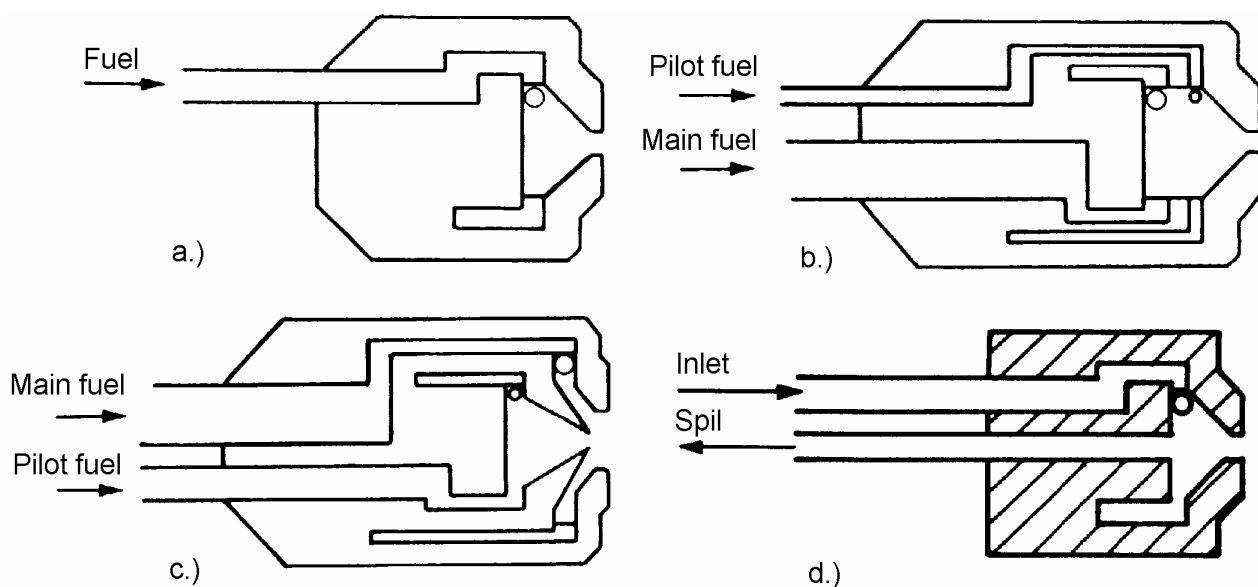


Fig. 12. Trends in atomizer design to overcome poor part load behaviour of simplex atomizer  
a.) Simplex ; b.) Duplex ;  
c.) Dual-orifice (duplex) ; d.) Spill-return

It is interesting to examine the axial and radial drop size distribution / separation in the spray.

Considering that air stream has higher tangential velocity than fuel the smaller diameter drops can be accelerated easier by the swirling air than heavier, bigger drops. The result of it is that the centrifugal force acting on each drop separates small drops from bigger drops so that fine droplets are located on a higher radius than big drops which are closer to the centre line.

Axially the situation is the opposite. The bigger drops are heavier and they have smaller surface to volume ratio which represents smaller aerodynamic resistance. The result is that bigger drops penetrate deeper into the combustion zone than small drops.

**b. Rotary atomizers**

In the rotary atomizer, liquid is fed onto a rotating surface where it spreads out fairly uniformly under the action of centrifugal force (see Fig. 14.). The rotating surface may take the form of a *flat disc*, *top*, *vaned disc*, *cup*, or *slotted wheel*. Diameters vary from 25 to 450 mm, the small discs rotating up to 60.000 rpm whereas larger discs rotate up to 12.000 rpm with atomizing capacities up to 1.4 kg/s. When coaxial air blast is used to assist atomization, lower speeds of the order of 3000 rpm may be used.

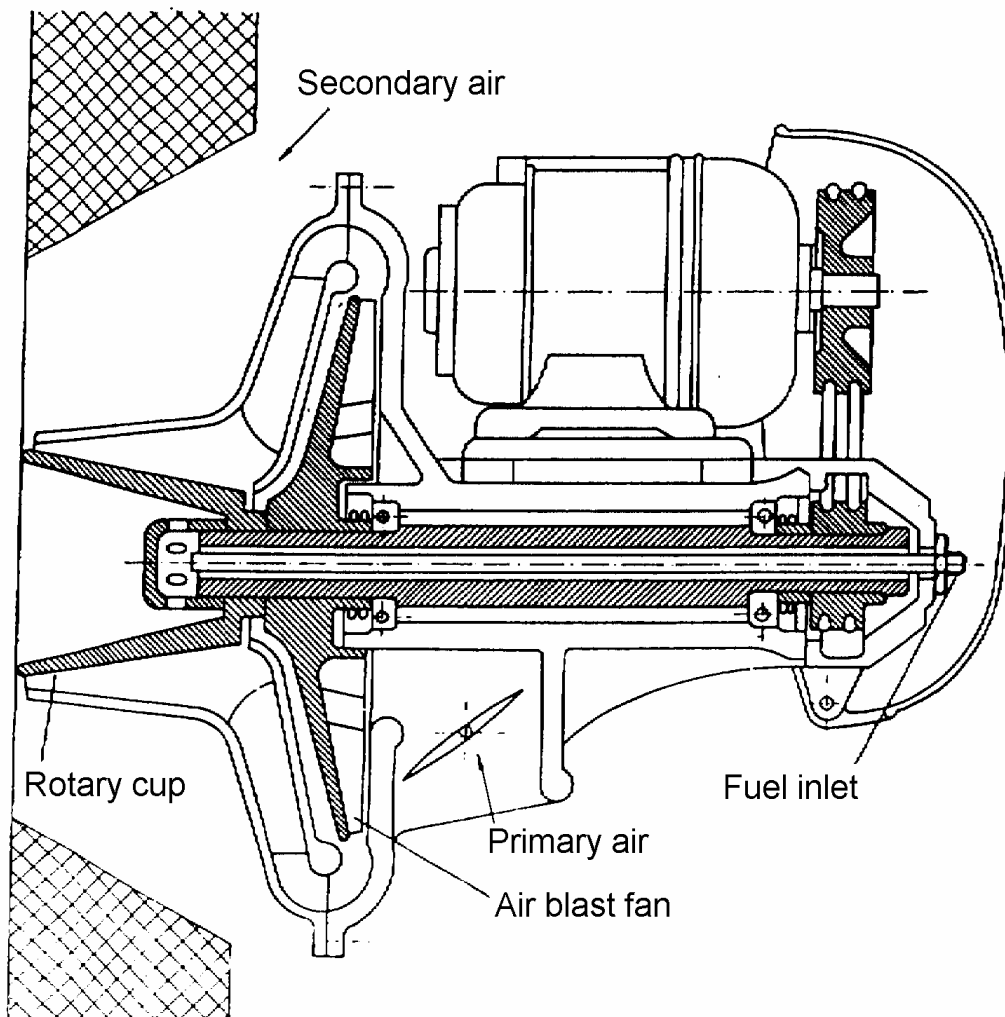


Fig. 14. Industrial burner equipped with rotary cup atomizer.

The system has extreme versatility and has been shown to atomize successfully liquids varying widely in viscosity. An important asset is that the thickness and uniformity of the liquid sheet can be readily controlled by regulating the liquid flow rate and the rotational speed.

Here again it is worth to examine the radial and axial droplet size distribution in the spray.

In this case the tangential velocity of liquid is proportional to the radius and so the tangential velocity is equal zero at the centre ( $c_{\text{tang}} = \text{const} \cdot r$ ).

The radial penetration proportionally depends only on the initial tangential velocity, and aerodynamic fly-velocity of drops. Because the latter is the function of the initial drop size, bigger drops locate on the outer ring of air stream, and smaller drops are in the centre.

### c. Twin-fluid atomization

The term twin-fluid atomization is used for systems in which a high-velocity gas stream is used to atomize fuel in a relatively low-velocity liquid fuel stream. The atomizing fluid is generally high pressure air, in gas turbine application, and high pressure steam in land-based and marine systems where steam is readily available from a boiler. From the point of view of combustion efficiency, air is preferable to steam, but the selection is based upon its availability and cost.

The specific terms "air blast", "steam blast" and "air-assist" are used in literature but the more general term is "twin-fluid atomization".

#### Air blast atomizer

This atomizer employs a simple concept in which the low pressure fuel is caused to flow over a plate located in a high velocity air stream. As the fuel flows over the edge of the plate (see Fig. 15.) it is atomized by the high velocity of air which then enters the combustion zone carrying the atomized fuel along with it.

As the fuel droplets are completely airborne, their distribution throughout the combustion zone is dictated by the air flow pattern.

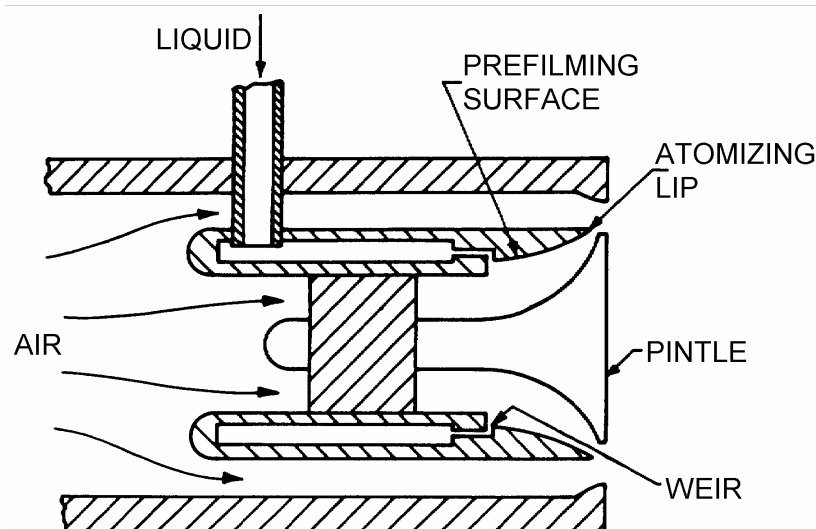


Fig. 15. Prefilming type of air blast atomizer

*Advantages*

- The fuel distribution pattern, which controls the combustion pattern remains fairly constant under all operating conditions.
- Absence of high fuel pressure required.
- Because the fuel enters the combustion zone premixed with air, the ensuing combustion is characterised by a blue flame of low luminosity (advantage in gas turbine application where we do not want the flame to lose energy by radiation) resulting a minimum exhaust smoke.

*Drawbacks*

- Incapable of stable operation at weak mixture strengths corresponding to low fuel flows.
- Poor atomization quality at start-up, when the chamber velocity is low, resulting unsatisfactory combustion performance.

**Air-assist atomizer**

This type of atomizer is essentially a pressure-swirl nozzle in which high velocity air is used to augment atomization at low fuel pressure.

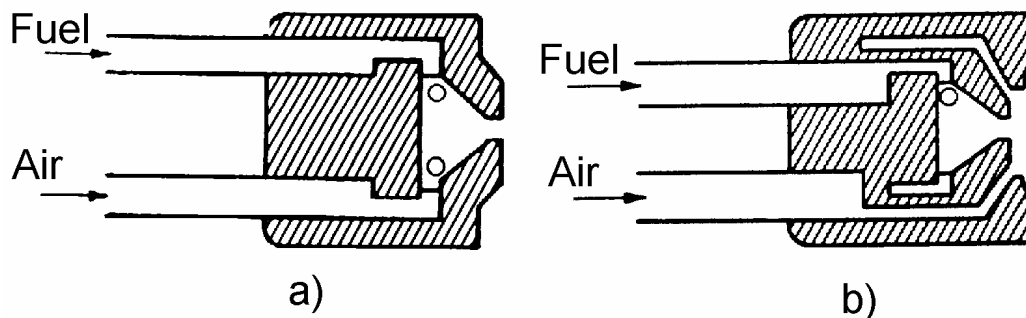


Fig. 16. Internal (a) and external (b) mixing air-assist atomizers.

When operating in the air-assist mode, it is basically the same as an air-blast atomizer. Its main difference stems from the fact that it uses air intermittently (usually only during start up), as opposed to the continuous air use of the air-blast atomizer. Furthermore, the air-assist nozzle uses a much higher air velocity which necessitates an external supply of air (major drawback in gas turbine application) or steam in case of industrial application (see Fig. 17).

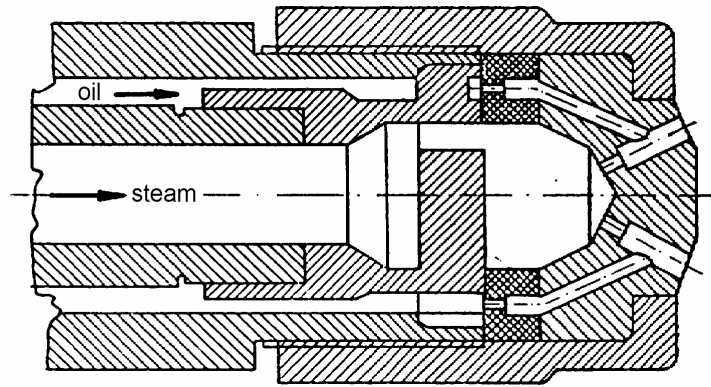


Fig. 17/a. Y-jet steam blast industrial atomizer

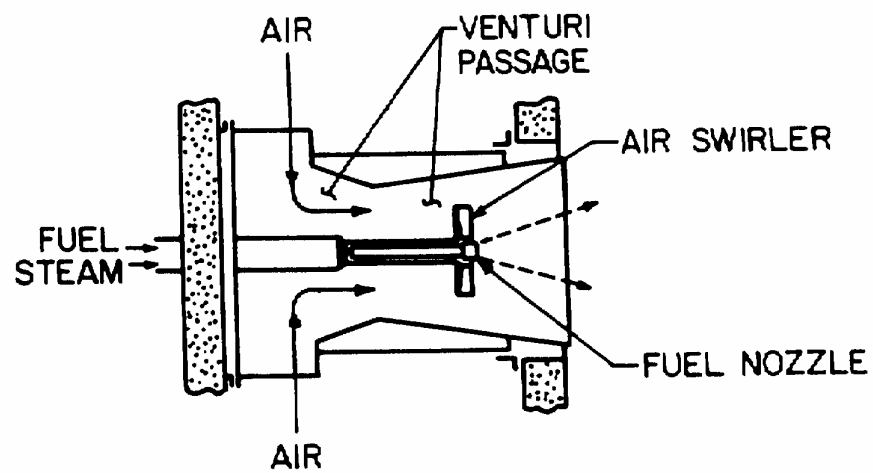


Fig. 17/b. Typical installation of Y-jet steam-blast fuel nozzle in burners

## STOICHIOMETRY

(PROBLEM SOLVING)<sup>2</sup>

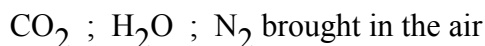
1. Determine the stoichiometric air/fuel ratio for a petrol approximating to hexane ( $C_6H_{14}$ ). Hence deduce the chemical equation if the petrol is burnt in 20 per cent excess air ( $\lambda = 1.2$ ), and the wet volumetric analysis of the products (a) if all the water vapour is present, and (b) if the products are cooled to an atmospheric pressure and temperature of 1 bar and 15 °C. Determine also dry volumetric analysis.

Finally estimate the chemical equation if only 80 per cent of air required for stoichiometric combustion is provided ( $\lambda = 0.8$ ).

### Solution

In case of stoichiometric combustion we assume that all the fuel molecules meet the required oxygen and reactions are complete and there is no intermediate species in the product gas.

Products of complete combustion:

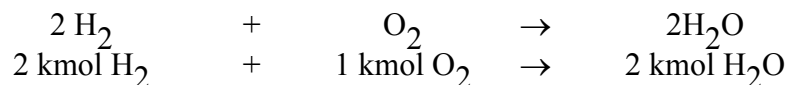


The determination of the molar (volume) analysis of the combustion products for the burning of hydrocarbon fuel in air is simple if the following rules are followed.

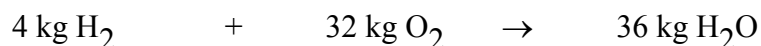
- a.) Find the number of kmols of oxygen required to burn all the hydrogen in the fuel to  $H_2O$  and all the carbon to  $CO_2$ .

e.g.

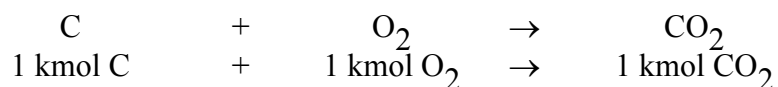
Stoichiometric burning of hydrogen.



or if mass balance is written using molecular weight of hydrogen and oxygen ( $M_H = 1.008 \text{ kg/kmol} \approx 1 \text{ kg/kmol}$  ;  $M_O = 16.000 \text{ kg/kmol}$ )



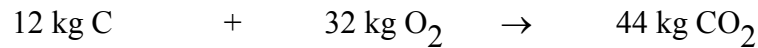
Stoichiometric burning of carbon.



and considering masses ( $M_C = 12.011 \text{ kg/kmol} \approx 12 \text{ kg/kmol}$ )

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<sup>2</sup> ref. G:\ROHALY\TXT\STOICH1.DOC



Summarising the above reactions:

Fuel		O <sub>2</sub> required	H <sub>2</sub> O produced	CO <sub>2</sub> produced
H <sub>2</sub>	1 kmol	0.5 kmol	1 kmol	-
	1 kg	8 kg	9 kg	-
C	1 kmol	1 kmol	-	1 kmol
	1 kg	32/12 = 2.67 kg	-	44/12 = 3.667 kg

- b.) Add nitrogen to both sides of the reaction equation, in the amount of 3.762 kmoles of nitrogen for each kmol of oxygen added.

In stoichiometric combustion calculations we assume the following air compositions.

	O <sub>2</sub>	N <sub>2</sub>
Volumetric analysis (m <sup>3</sup> ):	21.0 %	79.0 %
Gravimetric analysis (kg):	23.3 %	76.6 %

The volumetric analysis can be considered as molar analysis as well<sup>3</sup>. It means that 1 kmol of air contains 0.21 kmol of O<sub>2</sub> and 0.79 kmol of N<sub>2</sub>. It means that in air 79/21 kmol N<sub>2</sub> is added to 1 kmol of O<sub>2</sub>. (79/21 = 3.76190 ≈ 3.762)

Molar mass of nitrogen:  $M_N = 14.008 \text{ kg/kmol} \approx 14 \text{ kg/kmol}$

The mean molecular weight of air:

$$M_a = \frac{23.3 \cdot 32.0 + 76.6 \cdot 28.016}{100} = 28.92 \approx 29 \text{ kg / kmol}$$

- c.) Add excess air (oxygen and nitrogen in the above proportions) to both sides of the equation to the amount specified.

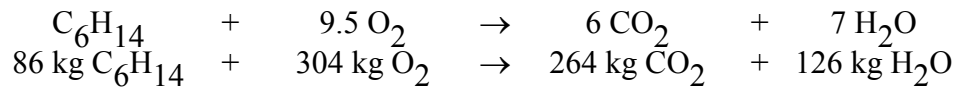
In this problem we have hexane (C<sub>6</sub>H<sub>14</sub>) as fuel. One kmole of hexane contains 6 carbon 14 oxygen atoms. Following the a.) rule above we need 6 kmol O<sub>2</sub> to burn all the carbons and 3.5 kmol O<sub>2</sub> to burn all the hydrogen in the fuel. Similarly, we can have the CO<sub>2</sub> and H<sub>2</sub>O kmols.

The stoichiometric (λ) reaction equation for burning 1 kmol of hexane.

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$$p_i \cdot V = n_i \cdot R_o \cdot T \quad \text{and} \quad p \cdot V = n \cdot R_o \cdot T \quad \text{give} \quad X_i = \frac{n_i}{n} = \frac{p_i}{p} = \frac{V_i}{V}$$

- <sup>3</sup> i: species (e.g. CO<sub>2</sub>); p<sub>i</sub>: partial pressure of species i;  
V<sub>i</sub>: partial volume of species i; X<sub>i</sub>: volume / mole fraction  
of species i



304 kg (9.5 kmol) oxygen is needed which is only 23.3 % (21.0 %) of the total requested air.

The total amount of air needed.

$$\begin{array}{cc} 304 \text{ kg (9.5 kmol) O}_2 & 23.3 \% (21.0 \%) \text{ of air} \\ \text{needed air} & 100.0 \% \text{ of air} \\ \hline \end{array}$$

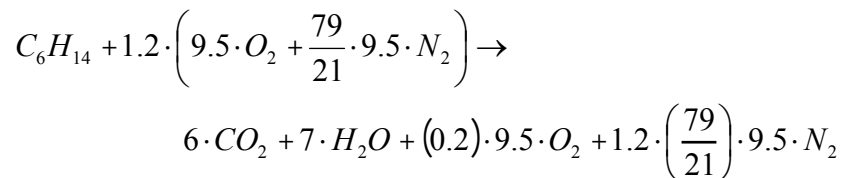
Needed air for stoichiometric combustion:

$$100 \cdot \frac{304}{23.3} = 1304.7 \text{ kg} \quad \left( 100 \cdot \frac{9.5}{21.0} = 45.2 \text{ kmol} \right)$$

Stoichiometric air/fuel ratio:

$$\mu_{\text{Lo}} = \frac{1304.7}{86} = 15.17 \text{ kg air / kg fuel}$$

If there is 20 per cent excess air, the reaction equation, including the nitrogen, becomes...



As you can see the excess air doesn't participate in any chemical reaction and can be found unchanged in the product gas. It means that we considered only stoichiometric reaction of hexane and oxygen.

The product composition gives the total kmole of the product.

- carbon-monoxide	(CO <sub>2</sub> )	:	n <sub>CO<sub>2</sub></sub>	=	6.00	kmol
- water vapour	(H <sub>2</sub> O)	:	n <sub>H<sub>2</sub>O</sub>	=	7.00	kmol
- oxygen	(O <sub>2</sub> )	:	n <sub>O<sub>2</sub></sub>	=	1.90	kmol
- nitrogen	(N <sub>2</sub> )	:	n <sub>N<sub>2</sub></sub>	=	42.89	kmol
<hr/>						
- TOTAL	:	n	=	57.79	kmol	

The *wet* volumetric analysis if all the water is present:

$$\text{a.)} \quad X_{\text{CO}_2} = 100 \cdot \frac{n_{\text{CO}_2}}{n} = 100 \cdot \frac{6.00}{57.79} = 10.38 \%$$

$$X_{\text{H}_2\text{O}} = 100 \cdot \frac{n_{\text{H}_2\text{O}}}{n} = 100 \cdot \frac{7.00}{57.79} = 12.11 \%$$

$$X_{\text{O}_2} = 100 \cdot \frac{n_{\text{O}_2}}{n} = 100 \cdot \frac{1.90}{57.79} = 3.29 \%$$

$$X_{\text{N}_2} = 100 \cdot \frac{n_{\text{N}_2}}{n} = 100 \cdot \frac{42.89}{57.79} = 74.22 \%$$

It is worth noting that more than 70 per cent of the product is nitrogen. It means that in most cases we can assume flue gas as nitrogen (e.g. when we use the specific heats of flue gas).

If the products are cooled to an atmospheric pressure and temperature of 1 bar and 15 °C, the volume/mole fraction of water vapour in the flue gas can be determined by the ratio of the partial pressure (this is the saturated pressure) of water at the given temperature and of the atmospheric/total pressure.

$$X'_{\text{H}_2\text{O}} \Big|_{1 \text{ bar}}^{15 \text{ }^\circ\text{C}} = 100 \cdot \frac{p_{\text{H}_2\text{O}}^{(15 \text{ }^\circ\text{C})}}{p} = 100 \cdot \frac{0.01704}{1.0} = 1.704 \%$$

If "y" is the total number of kilo moles of water vapour remaining in the products after cooling, the total amount of substance becomes  $n' = (n - n_{\text{H}_2\text{O}})_{\text{dry}} + y$  kmol.

$$X'_{\text{H}_2\text{O}} \Big|_{1 \text{ bar}}^{15 \text{ }^\circ\text{C}} = 100 \cdot \frac{y}{(n - n_{\text{H}_2\text{O}}) + y} = 1.704 \% \rightarrow y = 0.88 \text{ kmol}$$

The total amount of substance of products at 1 bar and 15 °C is

$$n' = (n - n_{\text{H}_2\text{O}})_{\text{dry}} + y = (57.79 - 7) + 0.88 = 51.67 \text{ kmol}$$

in the vapour state, and the *volumetric analysis* becomes:

$$\text{b.) } X'_{\text{CO}_2} = 100 \cdot \frac{n_{\text{CO}_2}}{n'} = 100 \cdot \frac{6.00}{51.67} = 11.61 \%$$

$$X'_{\text{H}_2\text{O}} = 1.70 \%$$

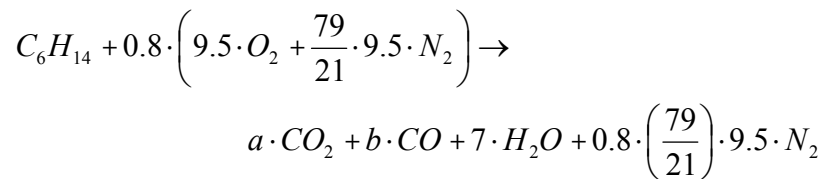
$$X'_{\text{O}_2} = 100 \cdot \frac{n_{\text{O}_2}}{n'} = 100 \cdot \frac{1.90}{51.67} = 3.68 \%$$

$$X'_{\text{N}_2} = 100 \cdot \frac{n_{\text{N}_2}}{n'} = 100 \cdot \frac{42.89}{51.67} = 83.01 \%$$

If all the vapour is assumed to be removed, say by a drying agent, the total amount of substance is 50.79 kmol, and the dry analysis is

$$X_{\text{CO}_2}^{\text{dry}} = 11.81 \% \quad X_{\text{H}_2\text{O}}^{\text{dry}} = 0.0 \% \quad X_{\text{O}_2}^{\text{dry}} = 3.74 \% \quad X_{\text{N}_2}^{\text{dry}} = 84.45 \%$$

When insufficient air is supplied for combustion, some of the carbon will burn to *carbon monoxide*, and there may also be some free hydrogen. Hydrogen, however, has greater affinity for oxygen than has carbon, and if the mixture is not too rich in fuel it is reasonable to *assume that all the hydrogen will be burnt*.



"a" and "b" is determined from element conservation law.

from the carbon balance,  $6 = a + b$

from the oxygen balance,  $0.8 \cdot 9.5 = a + \frac{b}{2} + \frac{7}{2}$

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$$a = 2.2 \text{ kmol}$$

$$b = 3.8 \text{ kmol}$$

2. A gaseous fuel has the following percentage composition by *volume*:

- methane	CH <sub>4</sub> :	26.6 %
- ethane	C <sub>2</sub> H <sub>6</sub> :	0.0 %
- propane	C <sub>3</sub> H <sub>8</sub> :	0.0 %
- Butane	C <sub>4</sub> H <sub>10</sub> :	0.0 %
- others	C <sub>m</sub> H <sub>n</sub> :	0.0 %
- carbon monoxide	CO :	12.6 %
- hydrogen	H <sub>2</sub> :	41.6 %
- carbon dioxide	CO <sub>2</sub> :	2.6 %
- nitrogen	N <sub>2</sub> :	14.7 %
- oxygen	O <sub>2</sub> :	1.9 %
- hydrogen sulphide	H <sub>2</sub> S :	0.0 %
- water vapour	H <sub>2</sub> O :	0.0 %

Find the wet volumetric and gravimetric (mass) analyses of the products of combustion when 10 per cent excess air is provided.

Solution

Reactants	kmol per kmol fuel	Stoichiometric reactions	kmol O <sub>2</sub> required	kmol CO <sub>2</sub> produced	kmol H <sub>2</sub> O produced
CH <sub>4</sub>	0.266	CH <sub>4</sub> + 2·O <sub>2</sub> → CO <sub>2</sub> + 2·H <sub>2</sub> O	2·0.266 = 0.532	0.266	0.532
CO	0.126	2·CO + O <sub>2</sub> → 2·CO <sub>2</sub>	0.126/2 = 0.063	0.126	—
H <sub>2</sub>	0.416	2·H <sub>2</sub> + O <sub>2</sub> → 2·H <sub>2</sub> O	0.416/2 = 0.208	—	0.416
CO <sub>2</sub>	0.026	—	—	0.026	—
N <sub>2</sub>	0.147	—	—	—	—
O <sub>2</sub>	0.019	—	-0.019 <sup>4</sup>	—	—
	1.000		0.784	0.418	1.248

Since 10 per cent excess air is provided, 0.0784 kmol of oxygen is additionally present and remains unchanged throughout the combustion process.

The total amount of nitrogen in the products is

$$1.1 \cdot \left(\frac{79}{21}\right) \cdot 0.784 + 0.147 = 3.3913 \text{ kmol/kmol fuel}$$

The *wet* analyses of the products by volume and by mass<sup>5</sup>:

Products (i)	kmol per kmol fuel (n <sub>i</sub> )	% by volume (V <sub>i</sub> /V = n <sub>i</sub> /n)	molecular weight kg/kmol (M <sub>i</sub> )	kg per kmol fuel (m <sub>i</sub> = n <sub>i</sub> · M <sub>i</sub> )	% by mass (m <sub>i</sub> )/m
CO <sub>2</sub>	0.4180	8.64	44	18.392	13.84
H <sub>2</sub> O	0.9480	19.60	18	17.064	12.84
O <sub>2</sub>	0.0784	1.62	32	2.5088	1.89
N <sub>2</sub>	3.3913	70.14	28	94.956	71.43
	4.8357	100.0		132.92	100.0

3. The analysis, by mass (gravimetric) of an anthracite fuel is 90 % carbon, 3 % hydrogen, 2 % oxygen, 1 % nitrogen and 4 % ash. Calculate the stoichiometric air-fuel ratio (kg/kg).

Given that the analysis of the *dry* combustion products, *by volume*, is 16.2 % CO<sub>2</sub>, 3.5 % O<sub>2</sub>, 80.3 % N<sub>2</sub>, calculate the excess air factor used.

<sup>4</sup> The oxygen in the fuel is assumed to be utilised totally during combustion and so the required amount of oxygen is decreased by this amount.

<sup>5</sup> Mass fraction of species "i":

$$Y_i = \frac{m_i}{m} = \frac{n_i \cdot M_i}{\sum_i n_i \cdot M_i} = \frac{(n_i \cdot M_i)/n}{\sum_i (n_i \cdot M_i)/n} = \frac{X_i \cdot M_i}{\sum_i X_i \cdot M_i} = \frac{(V_i/V) \cdot M_i}{\sum_i (V_i/V) \cdot M_i}$$

Also calculate the %  $\text{CO}_2$  in the dry stoichiometric products, and hence the ratio  $\frac{(X_{\text{CO}_2}^{\text{dry}})_s}{(X_{\text{CO}_2}^{\text{dry}} + X_{\text{CO}}^{\text{dry}})_\lambda}$ , which is an approximate formula for the excess air factor.

### Solution

Reactants	Molecular weight $M_i$ kg/kmol	kg per kg fuel	mol/kg fuel $\nu_i'$	mol $\text{O}_2$ required per kg fuel	mol $\text{CO}_2$ produced per kg fuel	mol $\text{H}_2\text{O}$ produced per kg fuel
C	12.011	0.90	74.931	74.931	74.931	—
$\text{H}_2$	2.016	0.03	14.881	7.441	—	14.881
$\text{O}_2$	32.000	0.02	0.625	-0.625	—	—
$\text{N}_2$	28.016	0.01	0.357	—	—	—
				81.747	74.931	14.881

kg  $\text{O}_2$  required for stoichiometric burning of 1 kg fuel:

$$m_{\text{O}_2} = 81.747 \cdot 10^{-3} \cdot M_{\text{O}_2} = 81.747 \cdot 10^{-3} \cdot 32 = 2.616 \text{ kg } \text{O}_2 / \text{kg fuel}$$

Amount of air required:

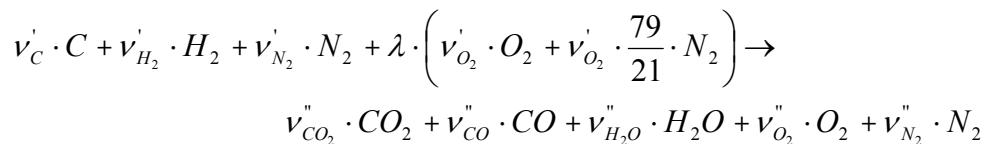
$$m_{\text{air}} = \frac{m_{\text{O}_2}}{0.233} = \frac{2.616}{0.233} = 11.23 \text{ kg air / kg fuel}$$

Because we calculated everything on the basis of one kg fuel the above amount of air is the air-fuel ratio as well.

Air-fuel ratio

$$\mu_{\text{LO}} = 11.23 \text{ kg air / kg fuel}$$

The combustion equation for non-stoichiometric case is



In the problem there is no CO in the products, therefore  $\nu_{\text{CO}}'' = 0$ .

$$\begin{aligned} \nu_C' &= 74.931 \text{ mol/kg fuel} & \nu_{\text{CO}_2}'' &= 74.931 \text{ mol/kg} \\ \nu_{\text{H}_2}' &= 14.881 \text{ mol/kg fuel} & \nu_{\text{H}_2\text{O}}'' &= 14.881 \text{ mol/kg} \\ \nu_{\text{N}_2}' &= 0.357 \text{ mol/kg fuel} & \nu_{\text{N}_2}'' &= \nu_{\text{N}_2}' + \lambda \cdot \nu_{\text{O}_2}' \cdot \frac{79}{21} \\ \nu_{\text{O}_2}' &= 81.747 \text{ mol/kg fuel} & \nu_{\text{O}_2}'' &= (\lambda - 1) \cdot \nu_{\text{O}_2}' \end{aligned}$$

Writing the definition of volume fraction on e.g.  $\text{CO}_2$  we can get the excess air factor directly.

$$X_{\text{CO}_2}^{\text{dry}} (= 0.162) = \frac{v_{\text{CO}_2}''}{v_{\text{CO}_2}'' + v_{\text{O}_2}'' + v_{\text{N}_2}''} = \frac{v_{\text{CO}_2}''}{v_{\text{CO}_2}'' + (\lambda - 1) \cdot v_{\text{O}_2}' + v_{\text{N}_2}' + \lambda \cdot v_{\text{O}_2}' \cdot \frac{79}{21}}$$

hence

$$\lambda = \frac{74.931 - 0.162 \cdot (74.931 + 0.357 - 81.747)}{0.162 \cdot 81.747 \cdot \left(\frac{79}{21} + 1\right)} = 1.205$$

$$\lambda = \frac{v_{\text{CO}_2}'' - X_{\text{CO}_2}^{\text{dry}} \cdot (v_{\text{CO}_2}'' + v_{\text{N}_2}' - v_{\text{O}_2}')}{X_{\text{CO}_2}^{\text{dry}} \cdot v_{\text{O}_2}' \cdot \left(\frac{79}{21} + 1\right)}$$

Now, we can check the above result with calculating the  $\text{O}_2$  and  $\text{N}_2$  volume fractions in the products, which are given.

$$v_{\text{N}_2}'' = v_{\text{N}_2}' + \lambda \cdot v_{\text{O}_2}' \cdot \frac{79}{21} = 0.357 + 1.205 \cdot 81.747 \cdot \frac{79}{21} = 370.92 \text{ mol / kg}$$

$$v_{\text{O}_2}'' = (\lambda - 1) \cdot v_{\text{O}_2}' = (1.205 - 1) \cdot 81.747 = 16.76 \text{ mol/kg}$$

The total mol number of the dry products:

$$n = v_{\text{CO}_2}'' + v_{\text{N}_2}'' + v_{\text{O}_2}'' = 74.931 + 370.920 + 16.760 = 462.611 \text{ mol / kg}$$

Dry volume fraction of  $\text{O}_2$  and  $\text{N}_2$  in the products

$$X_{\text{O}_2}^{\text{dry}} = 100 \cdot \frac{v_{\text{O}_2}''}{n^{\text{dry}}} = 100 \cdot \frac{16.760}{462.611} = 3.6 \%$$

$$X_{\text{N}_2}^{\text{dry}} = 100 \cdot \frac{v_{\text{N}_2}''}{n^{\text{dry}}} = 100 \cdot \frac{370.92}{462.611} = 80.2 \%$$

which compares favourably with the given values.

The volume fraction of  $\text{CO}_2$  in the stoichiometric products:

$$\begin{aligned} (X_{\text{CO}_2}^{\text{dry}})_s &= 100 \cdot \frac{(v_{\text{CO}_2}^{\prime\prime})_s}{(v_{\text{CO}_2}^{\prime\prime} + v_{\text{N}_2}^{\prime\prime})_s} = 100 \cdot \frac{(v_{\text{CO}_2}^{\prime\prime})_s}{\left(v_{\text{CO}_2}^{\prime\prime} + v_{\text{N}_2}^{\prime} + v_{\text{O}_2}^{\prime} \cdot \frac{79}{21}\right)_s} = \\ &= 100 \cdot \frac{74.931}{74.931 + 0.356 + 81.747 \cdot \frac{79}{21}} = 19.6 \% \end{aligned}$$

$$\frac{(X_{\text{CO}_2}^{\text{dry}})_s}{(X_{\text{CO}_2}^{\text{dry}})_\lambda} = \frac{19.6}{16.2} = 1.210$$

As we can see this formula is generally a good approximation (0.4 % rel. error), although the difference is greater with gaseous fuels.

4. The gravimetric analysis of a low rank lignite coal is 47.0 % C, 3.4 %  $\text{H}_2$ , 3.1 % S, 1.0 %  $\text{N}_2$ , 8.1 %  $\text{O}_2$ , 13.0 %  $\text{H}_2\text{O}$  (moisture), 24.4 % ash. Calculate the stoichiometric air fuel ratio ( $\mu_{\text{Lo}}$  kg air/kg coal), the stoichiometric flue gas amount produced by one kg of coal and draw the enthalpy - temperature diagram of the flue gas if the excess air in the furnace is 20 %.

Solution

Coal	kg per kg fuel (i)	Stoichio- metric reactions	kg O <sub>2</sub> required per kg fuel ( $\mu_{O_2}^m$ )	kg air required per kg fuel ( $\mu_{Lo}^m$ )	kg wet flue gas per kg fuel ( $\mu_{Vo}^{m,wet}$ )
C	0.470	$C + O_2 \rightarrow CO_2$	$[C] \cdot \frac{M_{O_2}}{M_C} = 0.470 \cdot \frac{32.000}{12.011} = 1.252$	$\frac{1.252}{0.233} = 5.373$	$[C] \cdot \frac{M_{CO_2}}{M_C} + \mu_{O_2,C}^m \cdot \frac{76.7}{23.3} = 5.844$
H <sub>2</sub>	0.034	$2 \cdot H_2 + O_2 \rightarrow 2 \cdot H_2O$	$[H_2] \cdot \frac{M_{O_2}}{M_{2H_2}} = 0.034 \cdot \frac{32.000}{4.032} = 0.270$	$\frac{0.270}{0.233} = 1.159$	$[H_2] \cdot \frac{M_{2H_2O}}{M_{2H_2}} + \mu_{O_2,H_2}^m \cdot \frac{76.6}{23.3} = 1.191$
S	0.031	$S + O_2 \rightarrow SO_2$	$[S] \cdot \frac{M_{O_2}}{M_S} = 0.031 \cdot \frac{32.000}{32.064} = 0.031$	$\frac{0.031}{0.233} = 0.133$	$[S] \cdot \frac{M_{SO_2}}{M_S} + \mu_{O_2,S}^m \cdot \frac{76.6}{23.3} = 0.164$
N <sub>2</sub>	0.010	—	—	—	0.010
O <sub>2</sub>	0.081	—	-0.081	$\frac{-0.081}{0.233} = -0.348$	$-0.348 \cdot 0.767 = -0.267$
H <sub>2</sub> O	0.130	—	—	—	0.130
ash	0.244	—	—	—	—
	1.000		<b>1.472</b>	<b>6.317</b>	<b>7.072</b>

The above calculations can be simplified by using constants which include the parameters of stoichiometric equations (e.g.  $M_{CO_2}/M_C$ ). In the following table you can find the relevant constants, and then the use of them is showed.

	$M_i$	$C_{O_2}^m$	$C_{L_o}^m$	$C_{CO_2}^m$	$C_{SO_2}^m$	$C_{N_2}^m$	$C_{V_o}^{m,dry}$	$C_{H_2O}^m$	$C_{V_o}^{m,wet}$
	kg/kmol	kg/kg fuel	kg/kg fuel	kg/kg fuel	kg/kg fuel	kg/kg fuel	kg/kg fuel	kg/kg fuel	kg/kg fuel
	Molecular weight	kg oxygen required per kg species $M_{O_2}/M_i$	kg air required per kg species $C_{O_2}^m/0.233$	kg carbon-dioxide $M_{CO_2}/M_C$	kg sulphur-dioxide $M_{SO_2}/M_S$	kg nitrogen $0.767 \cdot C_{L_o}^m$	kg dry flue gas $C_{CO_2,SO_2}^m + C_{N_2}^m$	kg water vapour $M_{H_2O}/M_{H_2}$	kg wet flue gas $C_{V_o}^{m,dry} + C_{H_2O}^m$
Carbon [C]	12.011	2.664	11.434	3.664	—	8.770	12.434	—	12.434
Hydrogen [H <sub>2</sub> ]	2.016	7.937	34.062	—	—	26.126	26.126	8.937	35.063
Sulphur [S]	32.064	0.998	4.283	—	1.998	3.285	5.283	—	5.283
Oxygen [O <sub>2</sub> ]	32.000	-1	-4.292	—	—	-3.292	-3.292	—	-3.292
Nitrogen [N <sub>2</sub> ]	28.016	—	—	—	—	1	1	—	1
Moisture	—	—	—	—	—	—	—	1	1
Ash	—	—	—	—	—	—	—	—	—

Constants in stoichiometrical calculation

- Stoichiometrically required oxygen per one kg of the specified fuel

$$\mu_{O_2}^m = \sum_i a_i \cdot C_{O_2,i}^m \left[ \frac{\text{kg oxygen}}{\text{kg fuel}} \right]$$

$a_i$  :  $i$ th species of the fuel based on *ultimate* analysis [kg/kg]

In our case...

$$\begin{aligned} \mu_{O_2}^m &= [C] \cdot C_{O_2,C}^m + [H_2] \cdot C_{O_2,H_2}^m + [S] \cdot C_{O_2,S}^m + [O_2] \cdot C_{O_2,O_2}^m = \\ &0.470 \cdot 2.664 + 0.034 \cdot 7.937 + 0.031 \cdot 0.998 + 0.081 \cdot (-1) = \\ &\underline{\underline{1.472 \text{ kg } O_2 / \text{ kg coal}}} \end{aligned}$$

Certainly, this value is equal with the calculated required oxygen amount in the table above.

- Stoichiometrically required air per one kg of the specified fuel (air-fuel ratio)

$$\mu_{Lo}^m = \sum_i a_i \cdot C_{Lo,i}^m \quad \text{or} \quad \mu_{Lo}^m = \frac{100}{23.3 (\%)} \cdot \mu_{O_2}^m \left[ \frac{\text{kg air}}{\text{kg fuel}} \right]$$

In our case...

$$\begin{aligned} \mu_{Lo}^m &= [C] \cdot C_{Lo,C}^m + [H_2] \cdot C_{Lo,H_2}^m + [S] \cdot C_{Lo,S}^m + [O_2] \cdot C_{Lo,O_2}^m = \\ &0.470 \cdot 11.434 + 0.034 \cdot 34.062 + 0.031 \cdot 4.283 + 0.081 \cdot (-4.292) = \\ &\underline{\underline{6.317 \text{ kg air / kg coal}}} \end{aligned}$$

or

$$\mu_{Lo}^m = \frac{100}{23.3 (\%)} \cdot 1.472 = \underline{\underline{6.318 \text{ kg air / kg coal}}}$$

- Stoichiometrically required *humid* air per one kg of the specified fuel

The above amount of air doesn't include the moisture content of air (humid air). It is possible with the following equation.

$$\mu_{Lo,H}^m = \mu_{Lo}^m \cdot (1 + X_{H_2O}^m) \left[ \frac{\text{kg humid air}}{\text{kg fuel}} \right]$$

$X_{H_2O}^m$ : absolute water content of air [kg/kg]

- Specific amount of carbon-dioxide produced

$$\mu_{\text{CO}_2}^m = \sum_i a_i \cdot C_{\text{CO}_2,i}^m \quad \left[ \frac{\text{kg CO}_2}{\text{kg fuel}} \right]$$

$$\mu_{\text{CO}_2}^m = [C] \cdot C_{\text{CO}_2,C}^m = 0.47 \cdot 3.664 = 1.722 \text{ kg CO}_2 / \text{kg coal}$$

- Specific amount of sulphur-dioxide produced

$$\mu_{\text{SO}_2}^m = \sum_i a_i \cdot C_{\text{SO}_2,i}^m \quad \left[ \frac{\text{kg SO}_2}{\text{kg fuel}} \right]$$

$$\mu_{\text{SO}_2}^m = [S] \cdot C_{\text{SO}_2,S}^m = 0.031 \cdot 1.998 = 0.062 \text{ kg SO}_2 / \text{kg coal}$$

- Specific nitrogen content of the flue gas

$$\mu_{\text{N}_2}^m = \sum_i a_i \cdot C_{\text{N}_2,i}^m \quad \left[ \frac{\text{kg N}_2}{\text{kg fuel}} \right]$$

$$\mu_{\text{N}_2}^m = [C] \cdot C_{\text{N}_2,C}^m + [H_2] \cdot C_{\text{N}_2,H_2}^m + [S] \cdot C_{\text{N}_2,S}^m + [O_2] \cdot C_{\text{N}_2,O_2}^m + [N_2] \cdot C_{\text{N}_2,N_2}^m =$$

$$0.47 \cdot 8.770 + 0.034 \cdot 26.126 + 0.031 \cdot 3.285 + 0.081 \cdot (-3.292) + 0.01 \cdot 1 =$$

$$4.855 \text{ kg N}_2 / \text{kg coal}$$

- Specific amount of dry flue gas

$$\mu_{\text{Vo}}^{m,\text{dry}} = \mu_{\text{CO}_2}^m + \mu_{\text{SO}_2}^m + \mu_{\text{N}_2}^m \quad \text{or} \quad \mu_{\text{Vo}}^{m,\text{dry}} = \sum_i a_i \cdot C_{\text{Vo},i}^{m,\text{dry}} \quad \left[ \frac{\text{kg exhaust}}{\text{kg fuel}} \right]$$

$$\mu_{\text{Vo}}^{m,\text{dry}} = 1.722 + 0.062 + 4.855 = 6.639 \text{ kg flue gas} / \text{kg coal}$$

or

$$\mu_{\text{Vo}}^{m,\text{dry}} = [C] \cdot C_{\text{Vo},C}^{m,\text{dry}} + [H_2] \cdot C_{\text{Vo},H_2}^{m,\text{dry}} + [S] \cdot C_{\text{Vo},S}^{m,\text{dry}} + [O_2] \cdot C_{\text{Vo},O_2}^{m,\text{dry}} + [N_2] \cdot C_{\text{Vo},N_2}^{m,\text{dry}} =$$

$$0.470 \cdot 12.434 + 0.034 \cdot 26.126 + 0.031 \cdot 5.283 + 0.081 \cdot (-3.292) + 0.010 \cdot 1 =$$

$$6.639 \text{ kg dry flue gas} / \text{kg coal}$$

- Specific water content of flue gas

$$\mu_{\text{H}_2\text{O}}^{\text{m}} = \sum_i a_i \cdot C_{\text{H}_2\text{O},i}^{\text{m}} \left[ \frac{\text{kg water vapour}}{\text{kg fuel}} \right]$$

$$\mu_{\text{H}_2\text{O}}^{\text{m}} = [\text{H}_2] \cdot C_{\text{H}_2\text{O},\text{H}_2}^{\text{m}} + [\text{H}_2\text{O}] \cdot C_{\text{H}_2\text{O},\text{H}_2\text{O}}^{\text{m}} =$$

$$0.034 \cdot 8.937 + 0.13 \cdot 1 = 0.434 \text{ kg water vapour / kg coal}$$

In more accurate calculation air humidity is taken into consideration as follows.

$$\mu_{\text{H}_2\text{O}}^{\text{m,H}} = \mu_{\text{H}_2\text{O}}^{\text{m}} + X_{\text{H}_2\text{O}}^{\text{m}} \cdot \mu_{\text{Lo}}^{\text{m}} \left[ \frac{\text{kg water vapour}}{\text{kg fuel}} \right]$$

- Specific amount of wet flue gas

$$\mu_{\text{Vo}}^{\text{m,wet}} = \mu_{\text{Vo}}^{\text{m,dry}} + \mu_{\text{H}_2\text{O}}^{\text{m(,H)}} \quad \text{or} \quad \mu_{\text{Vo}}^{\text{m,wet}} = \sum_i a_i \cdot C_{\text{Vo},i}^{\text{m,wet}} \left[ \frac{\text{kg exhaust}}{\text{kg fuel}} \right]$$

$$\mu_{\text{Vo}}^{\text{m,wet}} = 6.639 + 0.434 = 7.073 \text{ kg exhaust / kg coal}$$

or

$$\mu_{\text{Vo}}^{\text{m,wet}} = [\text{C}] \cdot C_{\text{Vo,C}}^{\text{m,wet}} + [\text{H}_2] \cdot C_{\text{Vo,H}_2}^{\text{m,wet}} + [\text{S}] \cdot C_{\text{Vo,S}}^{\text{m,wet}} + [\text{O}_2] \cdot C_{\text{Vo,O}_2}^{\text{m,wet}} +$$

$$[\text{N}_2] \cdot C_{\text{Vo,N}_2}^{\text{m,wet}} + [\text{H}_2\text{O}] \cdot C_{\text{Vo,H}_2\text{O}}^{\text{m,wet}} =$$

$$0.470 \cdot 12.434 + 0.034 \cdot 35.063 + 0.031 \cdot 5.283 + 0.081 \cdot (-3.292) +$$

$$0.010 \cdot 1 + 0.130 \cdot 1 = \underline{\underline{7.073 \text{ kg exhaust / kg coal}}}$$

### Enthalpy - temperature diagram of flue gas

Usually, enthalpy of working fluid is specified in terms of the unit mass of the given fluid. Here, due to practical reasons we specify enthalpy on the unit mass of fuel, in our case coal. It is more convenient because the input data of a furnace is its fuel consumption. Differentiation is useful and so we denote such an enthalpy by  $I_i$  ("i" species of flue gas).

- Specific enthalpy of stoichiometrically required air;  $I_{\text{air},o}(t)$

$$I_{\text{air},o}(t) = \mu_{\text{Lo}}^{\text{m}} \cdot \int_0^t C_{p,\text{air}}(t) \cdot dt = \mu_{\text{Lo}}^{\text{m}} \cdot C_{p,\text{air}}^o(t) \cdot t \left[ \frac{\text{kJ}}{\text{kg fuel}} \right]$$

where the mean specific heat capacity of air is calculated by

$$C_{p,air}^o(t) = \frac{1}{t_{[^\circ C]}} \cdot \int_0^{t_{[^\circ C]}} C_{p,air}(t) \cdot dt \quad \left[ \frac{\text{kJ}}{\text{kg K}} \right]$$

and is given in a table shown below.

- Specific enthalpy of stoichiometrically produced  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$

$$I_{\text{CO}_2}(t) = \mu_{\text{CO}_2}^m \cdot C_{p,\text{CO}_2}^o(t) \cdot t_{[^\circ C]} \quad \left[ \frac{\text{kJ}}{\text{kg fuel}} \right]$$

$$I_{\text{SO}_2}(t) = \mu_{\text{SO}_2}^m \cdot C_{p,\text{SO}_2}^o(t) \cdot t_{[^\circ C]} \quad \left[ \frac{\text{kJ}}{\text{kg fuel}} \right]$$

$$I_{\text{H}_2\text{O}}(t) = \mu_{\text{H}_2\text{O}}^m \cdot C_{p,\text{H}_2\text{O}}^o(t) \cdot t_{[^\circ C]} \quad \left[ \frac{\text{kJ}}{\text{kg fuel}} \right]$$

$$I_{\text{N}_2}(t) = \mu_{\text{N}_2}^m \cdot C_{p,\text{N}_2}^o(t) \cdot t_{[^\circ C]} \quad \left[ \frac{\text{kJ}}{\text{kg fuel}} \right]$$

- Specific enthalpy of stoichiometrically produced flue gas

$$I_{fg,o}(t) = I_{\text{CO}_2}(t) + I_{\text{SO}_2}(t) + I_{\text{H}_2\text{O}}(t) + I_{\text{N}_2}(t) \quad \left[ \frac{\text{kJ}}{\text{kg fuel}} \right]$$

- Specific enthalpy of flue gas including information on real combustion conditions (e.g. excess air -  $\lambda$ , flying ash content of flue gas)

$$I_{fg}(t) = I_{fg,o}(t) + (\lambda - 1) \cdot I_{air,o}(t) + I_{ash}(t) \quad \left[ \frac{\text{kJ}}{\text{kg fuel}} \right]$$

The specific enthalpy of ash in the flue gas assumes that ash temperature is equal with the gas temperature. The other needed information is the per cent of ash join the flue gas flow from the originally given ash content of the coal. We can consider the following per cents as empirical constants.

Flying ash in the flue gas of the original ash content of the fuel:

- Pulverised/dust coal and fluidised bed combustion:  $(1-b) = \underline{0.80} \dots 0.85$

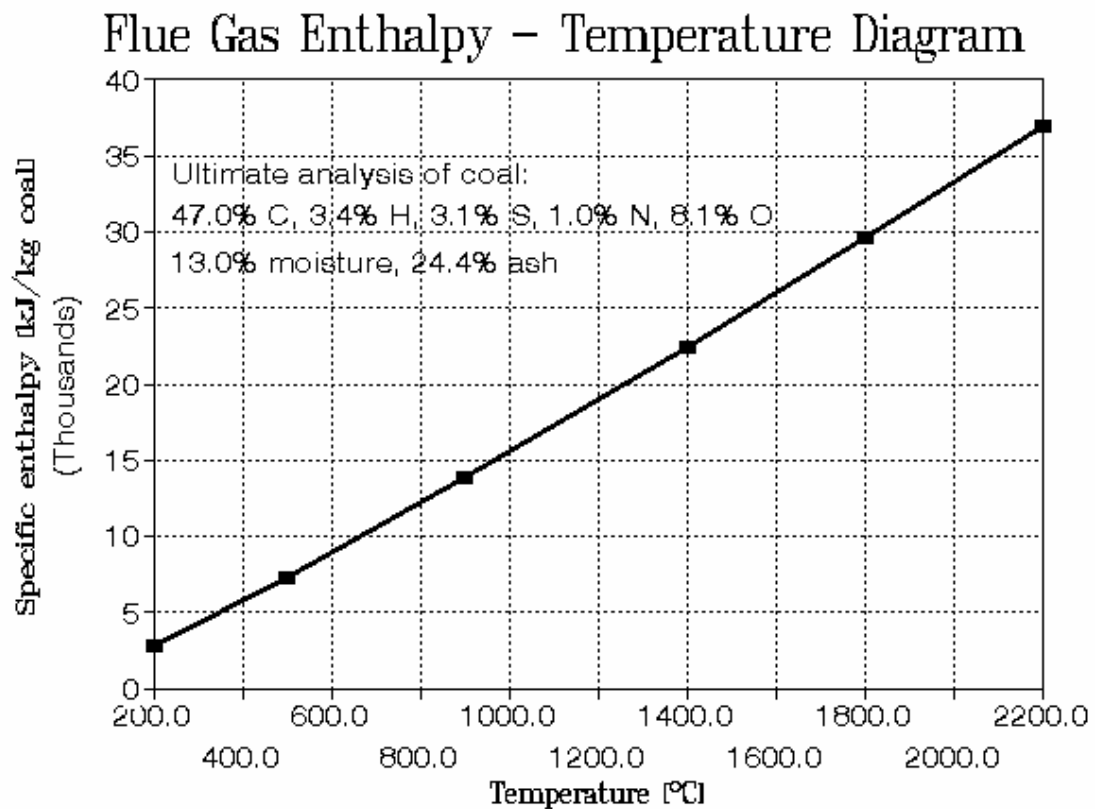
$$I_{ash}(t) = (1-b) \cdot [ash] \cdot C_{ash}^o(t) \cdot t \quad \left[ \frac{\text{kJ}}{\text{kg fuel}} \right]$$

Main specific heats at constant pressure  
( $C_{p,i}$ )

t	air	CO <sub>2</sub>	SO <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>	O <sub>2</sub>	ash
[°C]	[kJ/kgK]	[kJ/kgK]	[kJ/kgK]	[kJ/kgK]	[kJ/kgK]	[kJ/kgK]	[kJ/kgK]
0	1.004	0.815	0.607	1.859	1.039	0.915	
100	1.006	0.866	0.636	1.873	1.040	0.923	0.796
200	1.012	0.910	0.662	1.894	1.043	0.935	0.837
300	1.019	0.949	0.687	1.919	1.049	0.950	0.867
400	1.028	0.983	0.708	1.948	1.057	0.965	0.892
500	1.039	1.013	0.724	1.978	1.066	0.979	0.921
600	1.050	1.040	0.737	2.009	1.076	0.993	0.942
700	1.061	1.064	0.754	2.042	1.087	1.005	0.950
800	1.071	1.085	0.762	2.075	1.097	1.016	0.963
900	1.081	1.104	0.775	2.110	1.108	1.026	0.980
1000	1.091	1.122	0.783	2.144	1.118	1.035	1.005
1100	1.100	1.138	0.791	2.177	1.127	1.043	1.026
1200	1.108	1.153	0.795	2.211	1.136	1.051	1.051
1300	1.117	1.166	0.800	2.243	1.145	1.058	1.097
1400	1.124	1.178	- ↓ -	2.274	1.153	1.065	1.130
1500	1.131	1.189		2.305	1.160	1.071	1.185
1600	1.138	1.200		2.335	1.167	1.077	1.223
1700	1.144	1.209		2.363	1.174	1.083	1.298
1800	1.150	1.218		2.391	1.180	1.089	1.340
1900	1.156	1.226		2.417	1.186	1.094	1.382
2000	1.161	1.233		2.442	1.191	1.099	1.424
2100	1.166	1.241		2.466	1.197	1.104	1.466
2200	1.171	1.247		2.489	1.201	1.109	1.508
2500	1.184	1.264		2.554	1.214	1.123	1.550

The following table and graph show the results of the calculation of specific flue gas enthalpy versus temperature.

t	I <sub>air,o</sub>	I <sub>fg,o</sub>	I <sub>ash</sub>	I <sub>fg</sub>
[°C]	[kJ/kg]	[kJ/kg]	[kJ/kg]	[kJ/kg]
0	0	0	0	0
200	1278.56	1498.77	32.68	2810.01
500	3281.68	3911.58	89.89	7283.15
900	6145.81	7419.80	172.17	13737.78
1400	9940.43	12127.99	308.81	22377.23
1800	13076.19	16044.46	470.82	29591.47
2200	16273.86	20037.63	647.60	36959.09

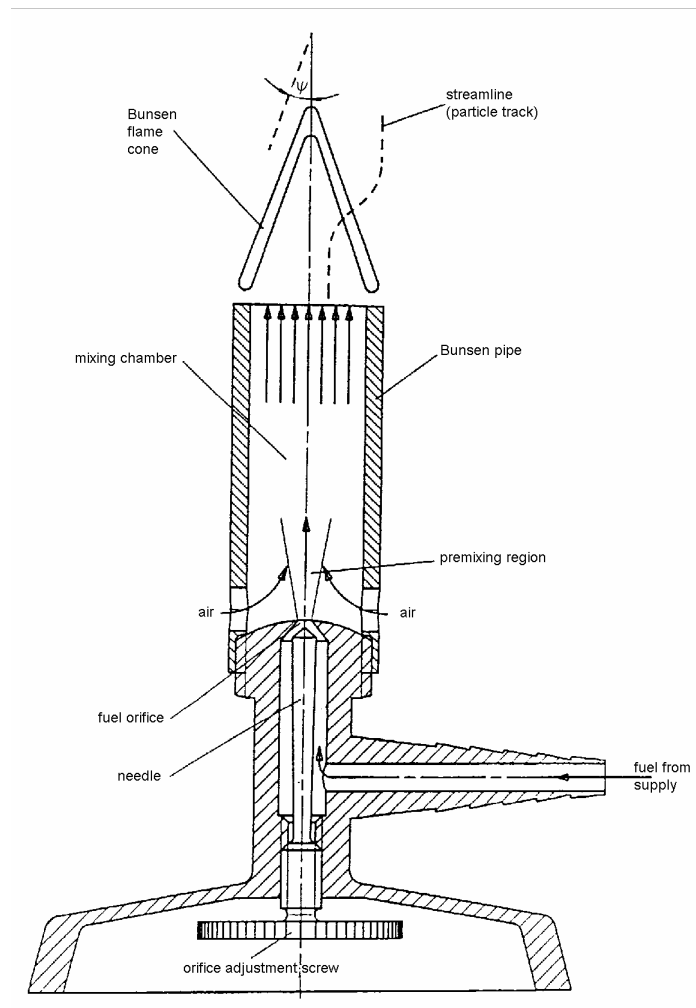


# COMBUSTION

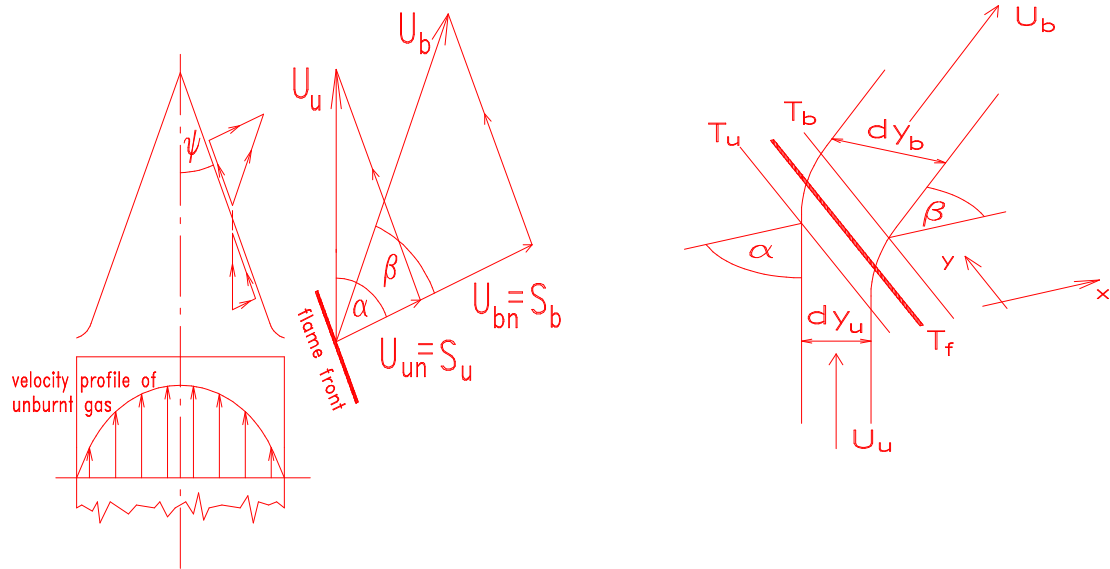
(Problem Solving<sup>6</sup>)

1. Determine the laminar burning velocity of a premixed fresh mixture containing 10 % methane and 90 % air by volume, if the half flame front cone angle on a Bunsen burner is measured as  $\psi = 30^\circ$ . The main velocity of the unburnt mixture is  $\overline{U}_u = 0.84 \text{ m/s}$ , and its temperature is  $T_u = 21.1^\circ\text{C}$ . The estimated pressure drop through the flame is  $(p_u - p_b) \approx 1/100 \text{ Hgmm}$ .

Calculate the velocity, density and temperature of the burnt gases, as well.



<sup>6</sup> ref. G:\ROHALY\TXT\HEATENG.DOC\COMBUST1.DOC

Solution**Laminar flame front on a Bunsen burner:**

Since the tangential forces are balanced the gases can accelerate only in direction normal to the flame front. It means, that stream lines remain parallel after the flame front.

Since the flame propagates normal to itself into the unburnt mixture, the burning velocity  $S_u$  is with respect to the unburnt mixture is defined as

$$S_u = U_{un}$$

in this steady state configuration. Since the Bunsen flame angle is denoted by  $\psi$  it follows that

$$U_{un} = U_u \cdot \sin(\psi)$$

and hence

$$S_u = U_u \cdot \sin(\psi)^7$$

Derivation of the required equation through the mass and momentum balance equations.

**Continuity equation on a stream tube**

$$\dot{m} = \rho_u \cdot U_{un} \cdot dl = \rho_b \cdot U_{bn} \cdot dl$$

Since stream lines are parallel

7

A particular phenomenon occurs at the *flame tip*. In case of close tip (general hydrocarbon flames) the burning velocity at the tip is normal and therefore equal to the flow velocity. It means that here the burning velocity is by a factor  $1/\sin(\psi)$  larger than the burning velocity through the oblique part of the cone. This can be explained by the strong curvature of the flame front at the tip leading to a preheating by the lateral parts of the flame front and thereby to an increase in burning velocity.

Close to the *rim* of the burner the *flame is detached*. This is due to conductive heat loss to the burner tube which leads, in regions very close to the rim, to temperatures at which combustion can not be sustained.

$$\rho_u \cdot U_{un} = \rho_b \cdot U_{bn}$$

Because the flow accelerates through the flame front ( $U_{un} < U_{bn}$ ) due to the thermal expansion ...

$$\rho_b < \rho_u$$

It can be showed that the bending of stream lines can be calculated from the density change.

$$\dot{m} = \rho_u \cdot U_u \cdot dy_u \quad \frac{dy_u}{dl} = \cos(\alpha) \quad U_{ut} = U_u \cdot \sin(\alpha)$$

$$\dot{m} = \rho_b \cdot U_b \cdot dy_b \quad \frac{dy_b}{dl} = \cos(\beta) \quad U_{bt} = U_b \cdot \sin(\beta)$$

Since  $U_{ut} = U_{bt}$  ...

$$\frac{\tan(\alpha)}{\tan(\beta)} = \frac{\rho_u}{\rho_b}$$

### Pressure drop due to momentum change

The balance equation in x direction (neglecting viscosious effects):

$$\rho \cdot U \cdot \frac{dU}{dx} = -\frac{dp}{dx}$$

$$\rho \cdot U \cdot dU = -dp$$

$$\rho \cdot U \Big|_{x \text{ direction}} = \rho_u \cdot U_{un} = \text{const.}$$

$$\int_{U_{un}}^{U_{bn}} \rho_u \cdot U_{un} \cdot du = - \int_{p_u}^{p_b} dp$$

$$\rho_u \cdot U_{un} \cdot (U_{bn} - U_{un}) = p_u - p_b$$

$$p_u - p_b = \rho_u \cdot U_{un} \cdot \left( \frac{\rho_u}{\rho_b} \cdot U_{un} - U_{un} \right) = \rho_u \cdot U_{un}^2 \left( \frac{\rho_u}{\rho_b} - 1 \right)$$

$$p_u - p_b = \rho_u \cdot U_{un}^2 \left( \frac{\rho_u}{\rho_b} - 1 \right)$$

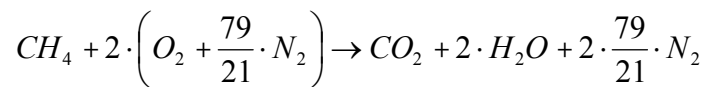
$$U_{bn} = U_{un} + \frac{p_u - p_b}{\rho_u \cdot U_{un}}$$

### Solution of the problem

The laminar burning velocity...

$$S_u = U_{un} = U_u \cdot \sin(\psi) = 0.84 \cdot \sin(30) = 0.42 \left[ \frac{m}{s} \right]$$

The stoichiometric reaction equation of methane and air...



The main molecular weight of fresh mixture...

$$\overline{M}_u = [CH_4] \cdot M_{CH_4} + [air] \cdot \overline{M}_{air} = 0.1 \cdot 16 + 0.9 \cdot 29 = 27.7 \left[ \frac{kg}{kmol} \right]$$

The density of unburnt mixture...

$$\rho_u = \frac{p_u \cdot \overline{M}_u}{R_o \cdot T_u} \quad R_o = 8314.3 \left[ \frac{J}{kmol \cdot K} \right]$$

$$p_u \cong p_{atm} + (p_u - p_b) = 10^5 + 1.334 \text{ [Pa]}$$

$$\rho_u = \frac{(10^5 + 1.334) \cdot 27.7}{8314.3 \cdot (21.1 + 273)} 1.133 \left[ \frac{kg}{m^3} \right]$$

The velocity of burnt gases...

$$U_{bn} = U_{un} + \frac{p_u - p_b}{\rho_u \cdot U_{un}} = 0.42 + \frac{1.334}{1.133 \cdot 0.42} 3.22 \left[ \frac{m}{s} \right]$$

The density of burnt gases...

$$\rho_b = \rho_u \cdot \frac{U_{un}}{U_{bn}} = 1.133 \cdot \frac{0.42}{3.22} 0.1476 \left[ \frac{kg}{m^3} \right]$$

Temperature of burnt gases...

$$T_b = \frac{p_b \cdot \overline{M}_u}{R_o \cdot \rho_b} = \frac{(10^5 - 1.334) \cdot 27.7}{8314.3 \cdot 0.1476} \cong 2257 \text{ [K]} = 1984 \text{ [}^\circ\text{C]}$$

The change of stream lines direction...

$$\varphi = \alpha - \beta$$

$$\alpha = 90^\circ - \psi = 90^\circ - 30^\circ = 60^\circ$$

$$\beta = \arctg \left[ \frac{U_{bt}}{U_{bn}} \right]$$

$$U_{bt} = U_{ut} = U_u \cdot \cos(\psi) = 0.84 \cdot \cos(30^\circ) = 0.7275 \left[ \frac{\text{m}}{\text{s}} \right]$$

$$\beta = \arctg \left[ \frac{0.7275}{3.22} \right] = 12.73^\circ$$

$$\varphi = 60^\circ - 12.73^\circ = 47.27^\circ$$

TECHNICAL UNIVERSITY OF BUDAPEST  
Department of Heat Engines

## PRACTICAL ANALYSIS OF COMBUSTION PRODUCTS

(laboratory measurement)<sup>8</sup>

### 1. The main objectives of measurement

When investigating the effectiveness of combustion plant it is often necessary to analyse the products experimentally. By taking samples at different stages of a reaction the combustion process can be studied, and the analyses can be used to discover lack of uniformity in fuel-air distribution. A products analysis (mainly CO<sub>2</sub> and O<sub>2</sub>) also enables the excess air factor (air/fuel ratio) to be computed in cases where direct measurement of the rate of air flow is not easily accomplished.

During the measurement we get acquainted with instruments and equipments capable to analyse combustion products of heat engines exhaust.

### 2. Principles of gas analysis

The constituents of interest in case of combustion are carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), oxygen (O<sub>2</sub>), nitric oxides (NO<sub>x</sub>), hydrocarbons (C<sub>x</sub>H<sub>y</sub>, CH<sub>4</sub>), sulphur dioxide (SO<sub>2</sub>), hydrochloric acid (HCl), soot and dust.

Instruments usually measure the concentration of the above gases in volume per cent, which doesn't depend on pressure and temperature if water is condensed before. We can convert this measure to other units, e.g. g/m<sup>3</sup>.

Usually, volumes (m<sup>3</sup>) are based on physical normal state which is T<sub>0</sub> = 273.15 K and p<sub>0</sub> = 1.01325 bar.

Very often the concentration given in volume per cent is too small, therefore parts per million is used instead of volume per cent.

The following table shows the conversion factors between different units (M<sub>i</sub> : molecular weight of the measured species i; p is in bar; T is in K of the sample gas)<sup>9</sup>

<sup>8</sup> Ref.: G:\ROHALY\TXT\EMISSION.DOC

<sup>9</sup> *Derivation of the conversion constants*

- Mass of gas - at pressure p and temperature T - having its density

$$m = \rho \cdot V \quad [\text{kg}]$$

as  $\rho$  [kg/m<sup>3</sup>] and volume as V [m<sup>3</sup>] is ...

- Density of gas can be calculated from the physical normal state as

(subscript o denotes the physical normal state) ...

$$\rho = \frac{\rho_o \cdot T_o}{p_o} \cdot \frac{p}{T}$$

- Density of gas at physical normal state is ...

$$\rho_o = \frac{M_i}{22.414} \frac{[\text{kg} / \text{kmol}]}{[\text{m}^3 / \text{kmol}]} = \left[ \frac{\text{kg}}{\text{m}^3} \right]$$

- Combining these equations gives ...

	1 v. %	1 ppm	1 mg/m <sup>3</sup>
1 v. %	1	10 <sup>4</sup>	$1.203 \cdot 10^5 \cdot M_i \cdot \frac{p}{T}$
1 ppm	10 <sup>-4</sup>	1	$12.03 \cdot M_i \cdot \frac{p}{T}$
1 mg/m <sup>3</sup>	$8.31 \cdot 10^{-6} \cdot \frac{T}{M_i \cdot p}$	$8.31 \cdot 10^{-2} \cdot \frac{T}{M_i \cdot p}$	1

### Conversion between wet and dry exhaust

The measurement are considered "dry" when the water content of the gas sample has been condensed out; otherwise, it is considered "wet". The water content represents the different between the "wet" and the "dry" results and is obtained by calculation or measurement to be agreed upon by the interested parties.

The conversion is carried out by using the following equation:

$$\varphi_{i,dry} = \varphi_{i,wet} \cdot \frac{1}{1 - \varphi_{H_2O}}$$

### Conversion to the particular exhaust gas oxygen level

To relate measurements to a standardized exhaust gas the following correction can be applied to give reference to a particular exhaust gas oxygen level.

The emission values as volumetric concentration of the component "i" related to oxygen volumetric concentration of e.g. 15 % in dry exhaust gas will be:

$$\varphi_{i,dry}^{15\%} = \frac{20.95 \% - 15 \%}{20.95 \% - \varphi_{O_2,dry}} \cdot \varphi_{i,dry} \quad (10)$$

Theoretically this correction can be applied to other oxygen levels and for "wet" and "dry" gases.

---


$$m = \frac{M_i}{22.414} \cdot \frac{T_0}{p_0} \cdot \frac{p}{T} \cdot V = \frac{273.15}{22.414 \cdot 1.01325} \cdot M_i \cdot \frac{p}{T} \cdot V = 12.03 \cdot M_i \cdot \frac{p}{T} \cdot V \quad [\text{kg}]$$

- If one wants to change volume per cent ( $\phi$ ) to [mg/m<sup>3</sup>] the following equation should be used ...

$$X_i = 12.03 \cdot M_i \cdot \frac{p}{T} \cdot \frac{\phi [\text{v.}\%]}{100} \cdot 10^6 = 1.203 \cdot 10^5 \cdot M_i \cdot \frac{p}{T} \cdot \phi \left[ \frac{\text{mg}}{\text{m}^3} \right]$$

<sup>10</sup> 20.95 % is the oxygen content of the dry ambient air.

### **3. Suitable sample handling system**

Emission measurement system is usually capable for simultaneous measurement of constituents. Setting up a system we have to consider

- sampling conditions and the transmission of sampling to the instruments,
- the placing of analysing instruments,
- calibration capabilities.

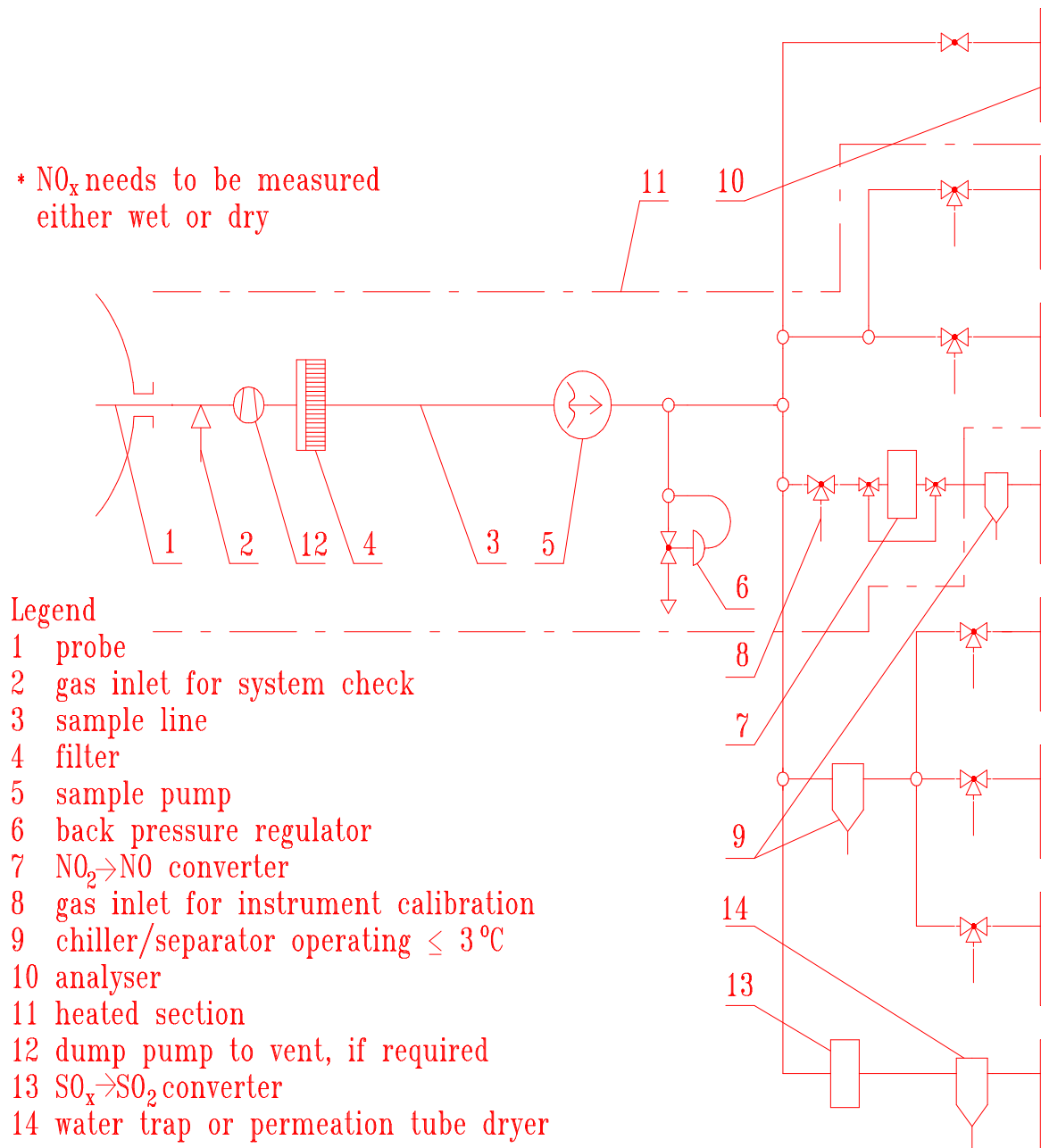


Fig. 1. Measurement system design for gaseous constituents  
Gas turbines exhaust gas emission measurement and evaluation  
ISO/TC 192/WG 2 No. 47

The composition of sample gas is not allowed to change during transmission and has to represent the gas flow we want to analyse. The task of sample preparation is to make the sample free of disturbing constituents, such as particles, water vapour, disturbing gases.

The gas and solid phase constituents are sampled separately. A principal system, containing the important components is shown in Fig. 1. First the sample is passed through a heated filter. At this moment the water vapour in the sample is not allowed to condensate, so the tube is heated as well.

Selection of sampling tube material is also important, because it can not cause any chemical transformation and can not behave as a catalysator. Using stainless steel (or equivalent) tubes only is not practical and instead of it tubes with ceramic lining is built into the system. PTF (teflon) can be used, as well, if the temperature allows it.

The water vapour is condensed in an electronic cooler, where the gas cooled down to 2 - 4 °C temperature. It is necessary because most instruments are sensitive to water and on the other hand the presence of water vapour falsifies the results. It is worth noting that carbon dioxide, sulphur dioxide and a part of nitrix oxides are soluble in water.

The pipe lines have to be as short as possible to avoid ad- and absorption. PTFE (Poly-Tetra-Fluor-Ethylene) is the best material to transmit sample gas because its wall is inert.

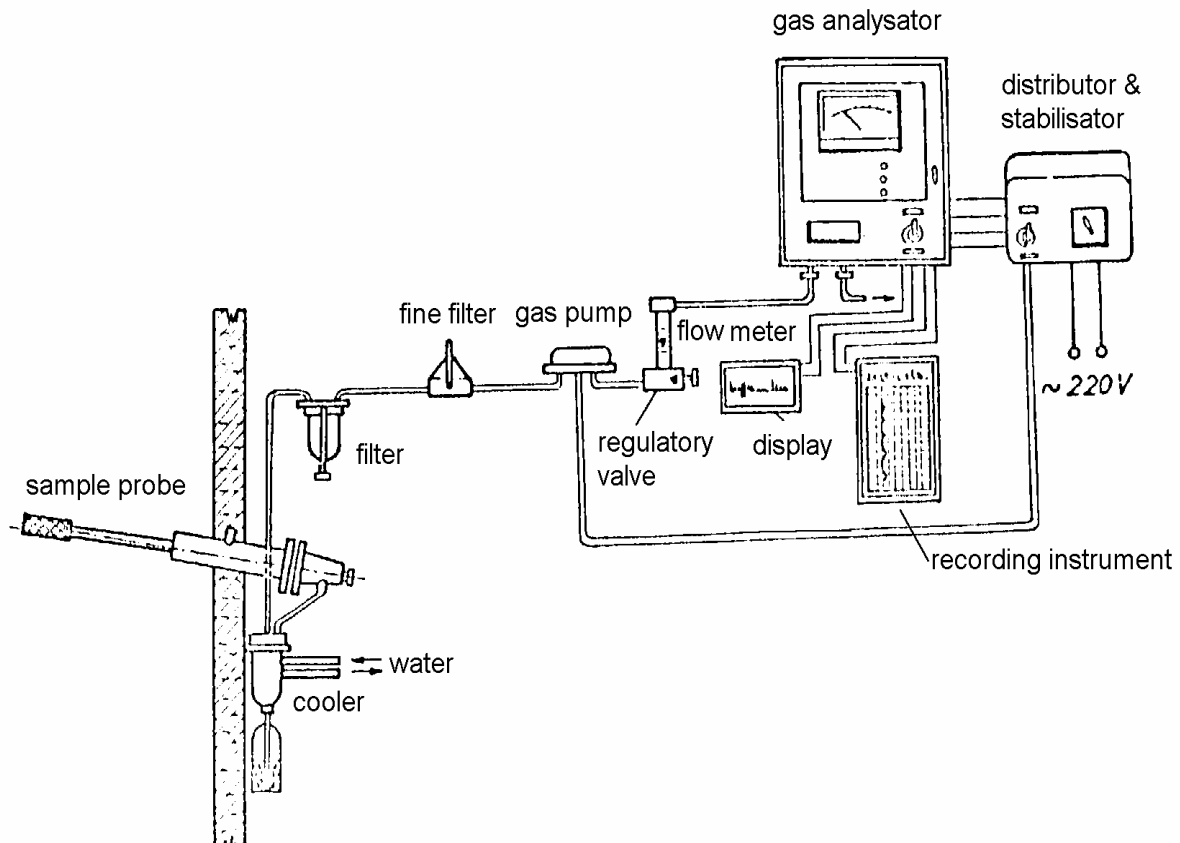


Fig. 2. Industrial gas analyser system

Generally, a membrane pump and a fine filter can be found after the cooling equipment. Before the sample reaches the analysing instruments it passes a volume flow rate measuring equipment. If it is possible the analysers are connected serially and the sample passes the instruments each after each other which ensures to determine belonging species.

The instruments have to be protected against weather and the best is to place them in a space where the temperature is constant.

The instruments have to be calibrated with a known composition gas before, during and after the measurement in order to set and/or check them.

#### 4. Gas analysers

Instruments for each constituents can analyse the sample by continuous or repeated way. The analysis can be done by chemical means, by physical means and both.

#### Instruments based on absorption of the constituents

#### Instruments based on chemical processes and physical behaviours

Chemical reactions taking place before measuring any physical behaviour of the system allow us to determine very low concentrations of combustible gases in the sample. The physical parameter to be measured is the temperature change of the system which is proportional with the combustible content of sample.

The ELKON S105 instrument is capable to determine the CO content of spark ignition internal combustion engine exhaust gases. The combustible gases in the sample burn passing through the high temperature (450 - 500 °C) platinum catalyser. The released heat increases the temperature of the catalyser which is measured as the resistance change of the sample arm in an out-of-balance Wheatstone bridge, Fig.5. The reference resistance is also a platinum wire surrounding by air.  $R_1$  and  $R_2$  are constant resistances, insensible to temperature change.

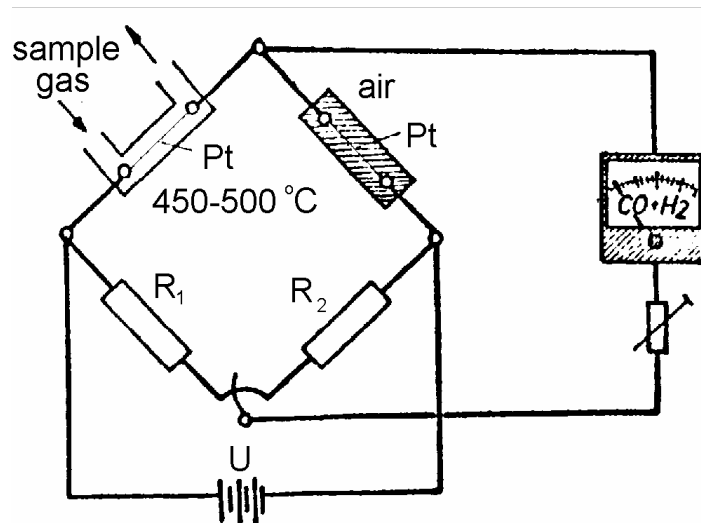


Fig. 5. Combustible analyser based on measuring released heat

#### CO<sub>2</sub> measurement by the thermal conductivity variations

When a heated wire is placed in a gaseous atmosphere it loses heat by radiation, convection and *conduction*. If the losses by radiation and convection are kept constant, the total heat loss is dependent on the heat loss by conduction, which varies with the constituents of the gas since each has a different and characteristic thermal conductivity.

If a constant heat input is supplied to the wire (100 - 150 °C) there is an equilibrium temperature for each mixture, and if CO<sub>2</sub> content alone is varied then its concentration will be indicated by a measurement of the temperature of the wire.

In an actual instrument the heat loss from the wire is mainly by *conduction*, the other means<sup>11</sup> account for about 1 % each of the total loss. The convection loss is reduced by mounting the wire vertically. The instrument is calibrated against mixtures of known composition.

The schematic layout on Fig. 6 shows the operation of such instrument. The sample of gas is passed over an electrically heated platinum wire in a cell which forms one arm of a Wheatstone bridge. In another arm of the bridge is a similar cell containing air. A difference in CO<sub>2</sub> content between the two cells causes a difference in temperature between the two wires and hence a difference in resistance. The higher the CO<sub>2</sub> content of the sample the lower its heat conductivity which results less cooling of the wire. The out-of-balance potential of the bridge is measured by a recording potentiometer, calibrated to give CO<sub>2</sub> content directly.

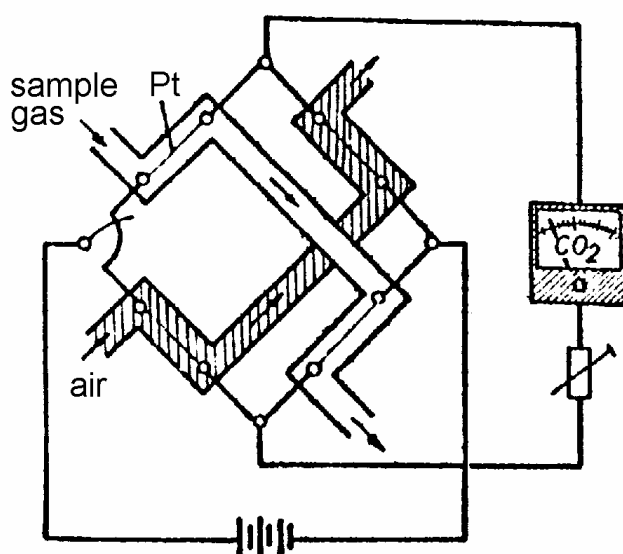


Fig. 6. CO<sub>2</sub> analyser by the thermal conductivity variations

#### Combined CO<sub>2</sub>, CO+H<sub>2</sub> analyser

The above two instruments can be linked together to determine CO+H<sub>2</sub> (by measurement of heat release during burning of CO+H<sub>2</sub>) and CO<sub>2</sub> concentrations (by thermal conductivity variations). Fig. 7 shows the schematic layout of such system, namely instrument TZ 2.

The sample is sucked by the pump and reaches the three way valve through the sampling probe and the rough filter. From time to time air is induced through the three way valve to calibrate the system. SO<sub>2</sub> has to be extracted from the sample because it falsifies the measurement (1 % SO<sub>2</sub> is equal with ~2 % CO<sub>2</sub>). Iron turnings are used for this purpose. The cleanliness of the sample can be checked manually through the glass window after the gas cooler (condensing water vapour and/or ensuring required temperature).

<sup>11</sup> e.g. convection, radiation, end cooling, diffusion

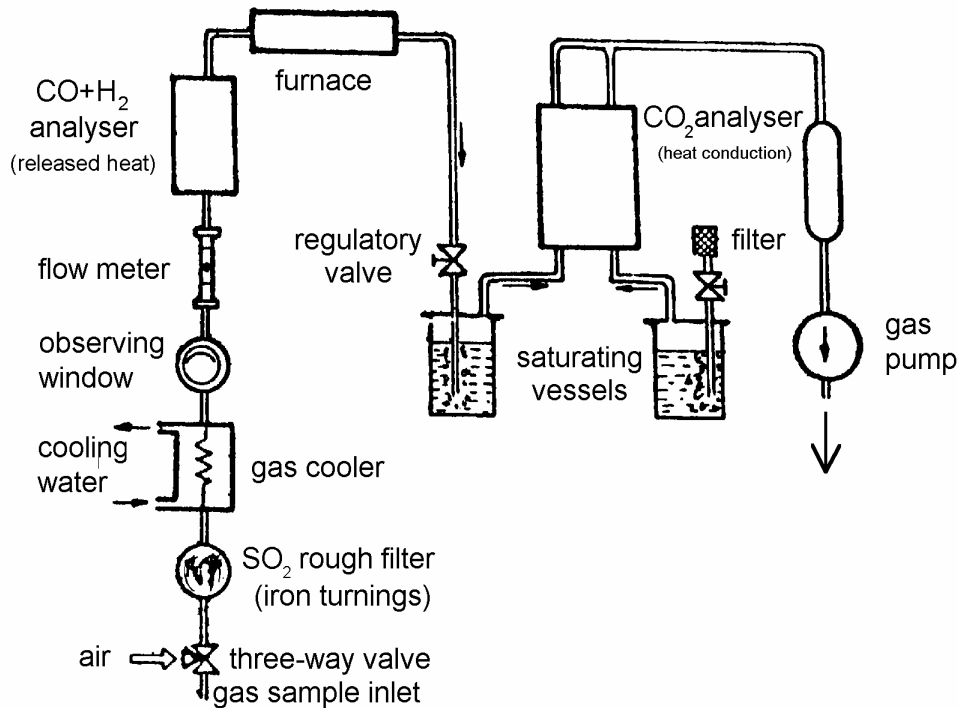


Fig 7. Combined  $\text{CO}_2$ ,  $\text{CO}+\text{H}_2$  analyser system

The required mass flow rate is adjusted by the control valve. After the flow-meter the sample is drawn into the above explained  $\text{CO}+\text{H}_2$  analyser. It catalytically burns the  $\text{CO}+\text{H}_2$  content of the sample and the released heat is measured by the resistance change of a platinum wire causing out-of-balance potential of a Wheatstone bridge. The subsequent part of the system is a furnace where the other combustibles ( $\text{C}_x\text{H}_y$ ) are burnt. Then the sample is cooled down and saturated by water in a saturating vessel and introduced into the  $\text{CO}_2$  analyser. It measures the total  $\text{CO}_2$  content of the sample, including  $\text{CO}_2$  formed in the  $\text{CO}+\text{H}_2$  analyser, by thermal conductivity variations which causes an out-of-balance potential of the Wheatstone bridge.

The amount of  $\text{CO}_2$  in the original sample can be calculated from its measured  $\text{CO}+\text{H}_2$  content.

### Colorimetric instruments

Gases can react with other materials so that the colour of the product is different compared to the original colour of the material. The change can be sudden or proportional to the gas concentration. In both cases the discolouration is measured and determined to be proportional to the relevant constituents.

#### *Dräger probe*

The sample gas is sucked through a thin tube (7-8 mm diameter; 10-12 cm length) filled with a solid phase, crystal or dust form material depending on the constituent to be analysed (See Fig. 8.). The length of discolouration of the reagent gives the concentration of the relevant species in the sample. The scale on the tube gives the concentration. Certainly, the amount of sucked gas is well determined. To ensure this the *cartridge* is

fitted to a constant volume, manual pump, with which the prescribed volume is sucked through the probe once or more times.

Considering the required conditions the error of measurement is around 5...30 % based on the readable value on the tube. One probe can be used only once.

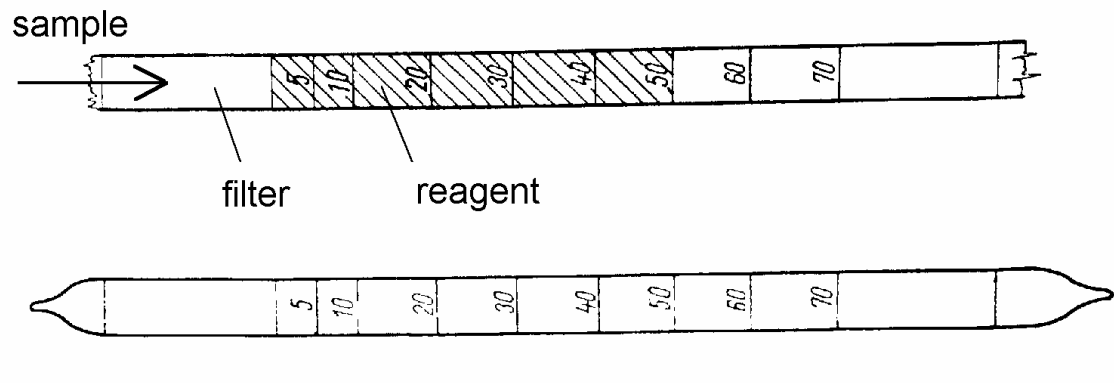


Fig. 8. Dräger probe

#### Gas analysis by infra-red spectra

For the most part gases are transparent to electromagnetic radiation. However, at certain frequencies, the energy associated with a photon coincides with that required to change a molecule from one quantized energy level to another. At those frequencies a gas will *absorb* radiation.

Combustion products absorb radiation in the *infrared* portion of the spectrum (See Fig. 9). The transmittance of  $\text{CO}_2$  and of  $\text{CO}$  over the range of  $3.5 < \lambda < 5$  microns. Notice that  $\text{CO}_2$  absorbs at about 4.2 microns; whereas  $\text{CO}$  absorbs at about 4.6 microns. Thus by using a radiation detector with a sensitivity as shown, one can detect  $\text{CO}_2$  in a sample without interference from any carbon monoxide that may also be present<sup>12</sup>.

<sup>12</sup> This method is suitable for carbon monoxide, carbon dioxide, sulphur and nitrogen compounds, methane and other hydro carbons, and organic vapours.

Oxygen, hydrogen, nitrogen, argon, chlorine, and helium, do not absorb infra-red radiation and so will not be detected by this type of instrument.

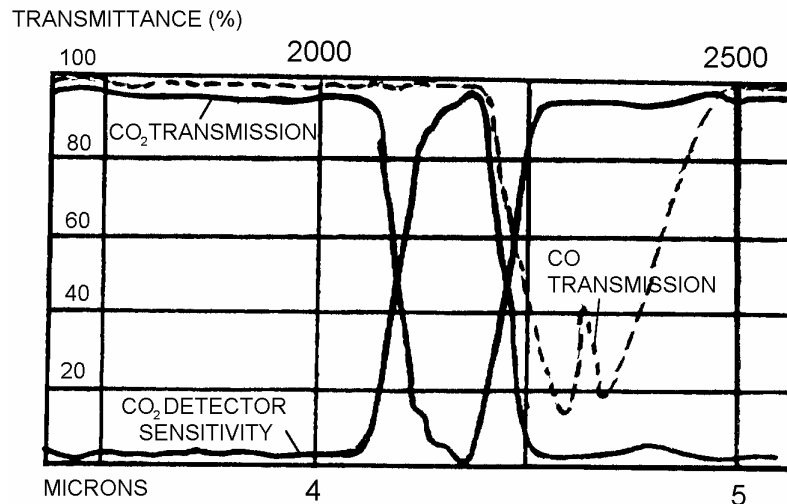


Fig. 9. Per cent transmittance of  $\text{CO}_2$  and CO in the infrared portion of the spectrum

Referring to fig. 10, the gas being analysed is continuously passed through a sample cell ( $M_1$ ). A reference cell ( $M_2$ ) containing a non absorbing background gas, e.g. nitrogen. The detector chambers ( $Er_1$ ,  $Er_2$ ) contain pure samples of the constituent to be detected. Radiation from infrared source (broad band) is passed through the two cells ( $M_1$ ,  $M_2$ ) and then to the detector chambers ( $Er_1$ ,  $Er_2$ ) where it is absorbed. The subsequent heating of the gases in  $Er_1$  and  $Er_2$  causes an increase in pressure in the two chambers. Detector chambers are separated by a thin metal diaphragm which, together with an insulated, perforated plate, forms a capacitor.

The detector,  $Er_1$  will absorb less radiation than  $Er_2$  because of the attenuation in the sample cell,  $M_1$  causing a diaphragm to deflect in proportion to the difference in the rates of energy absorption due to greater pressure in  $Er_2$ . The displacement of the diaphragm produces a change in capacitance of the condenser and a current is produced which is amplified to give a reading on a micro-ammeter. The micro-ammeter scale is calibrated to give the corresponding concentration of the constituent in the gas being analysed.

To avoid zero errors the radiation is cut off from both tubes simultaneously and allowed to fall on them simultaneously, by means of a vane (B) which rotates at a low frequency. The pressure changes are then related to the temperature changes produced by the differential absorption in detector  $Er_1$  and  $Er_2$ .

Interferences from gases with overlapping absorption bands may be minimized by gas absorption filters and/or optical filters.

The instrument is calibrated against accurately prepared samples of gas mixture.

The following lower limits are quoted in parts per million for the most common applications:

$\text{CO}_2$  : 3 ppm;      CO, and  $\text{C}_2\text{H}_4$  : 10 ppm;  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_6$  : 20 ppm

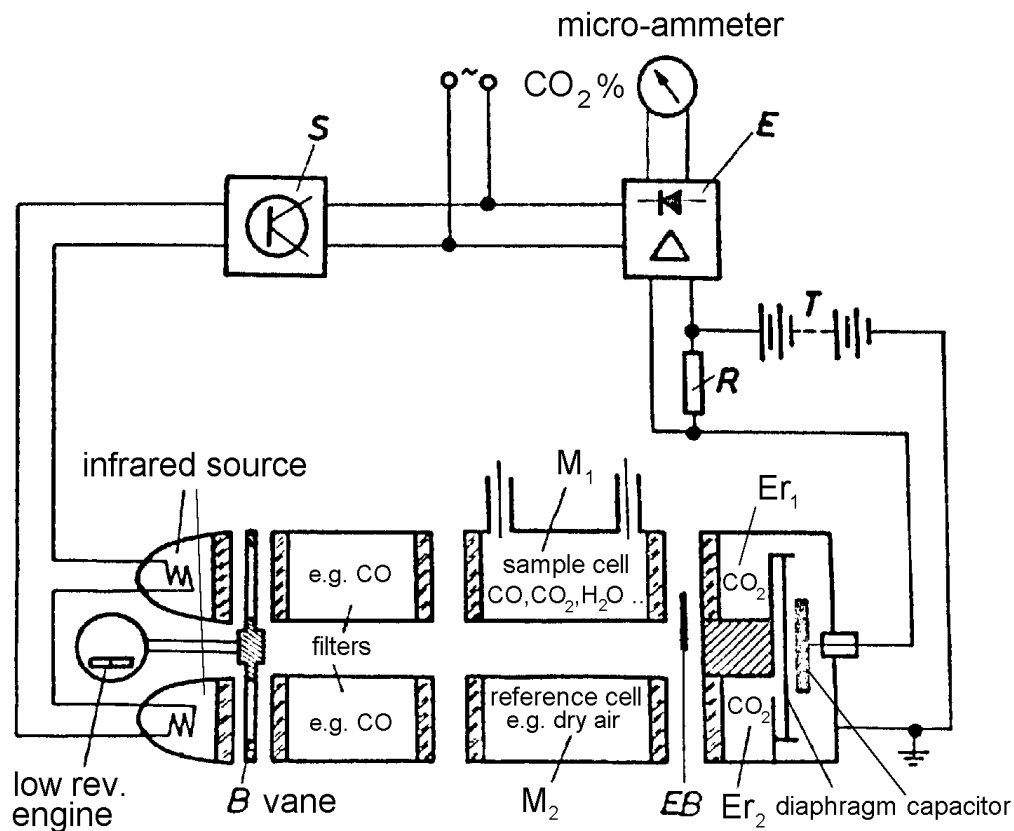


Fig. 10. Infra-red gas analyser

Oxygen measurement by magnetic means

(Annulus-chamber oxygen analyser)

Gases may be classified in two groups:

- (a) *Diamagnetic* gases which seek the weakest part of a magnetic field.
- (b) *Paramagnetic* gases which seek the strongest part of magnetic field.

Most gases are diamagnetic, but oxygen is paramagnetic, and this property of oxygen can be utilised in measuring the oxygen content of gas mixtures. The magnetic susceptibility of oxygen is reversally proportional with absolute temperature, and this behaviour is utilised in the following instrument.

Referring to Fig. 11. the gas sample is introduced into the analysis cell and passes through the annulus as shown. The two sides of the annulus is connected with a horizontal cross-tube. At one side (left in this case) of the cross-tube is located between a large permanent magnet having a high intensity magnetic field. Two electrically heated identical platinum resistance are coiled around the cross-tube and they are connected in adjacent arms of a Wheatstone bridge.

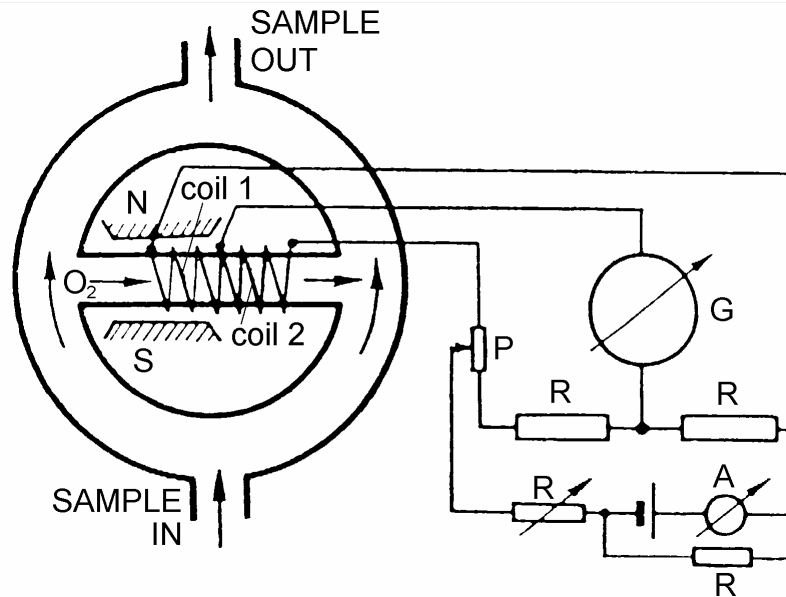


Fig. 11. Magnetic oxygen analyser

When the gas sample, introduced into the annulus, contains paramagnetic constituent, like oxygen, it is drawn into the cross-tube. The paramagnetic susceptibility of oxygen decreases because it is heated by coil "1", which means that fresh and cold gases, which have higher magnetic susceptibility, push the gas content of the cross-tube forward and hence continuous flow is established (sometimes called the "magnetic breeze"). The gas heated by coil "1" gives this heat energy to coil "2". It means that coil "1" gets cool and coil "2" become warmer which results that their electric resistance change and the Wheatstone bridge goes out of balance. The resulting electro-motoring-force is measured by a potentiometer, and since this is proportional to the oxygen content, the reading gives the oxygen content of the mixture.

#### Hydrocarbon detection by flame ionization

The preferred technique for hydrocarbon detection is the flame ionization method. Introduction of hydrocarbons into a hydrogen air flame produces, an a complex process, electrons and positive ions. By burning the sample in an electric field it is possible to count these ions which are indicative of the number of carbon atoms introduced into the flame.

An example of such a burner is shown in Fig. 12. The sample is mixed with the hydrogen-diluent fuel and burned in a diffusion flame. The combustion products pass between electrode. An ion current is established and detected to indicate hydrocarbon concentration.

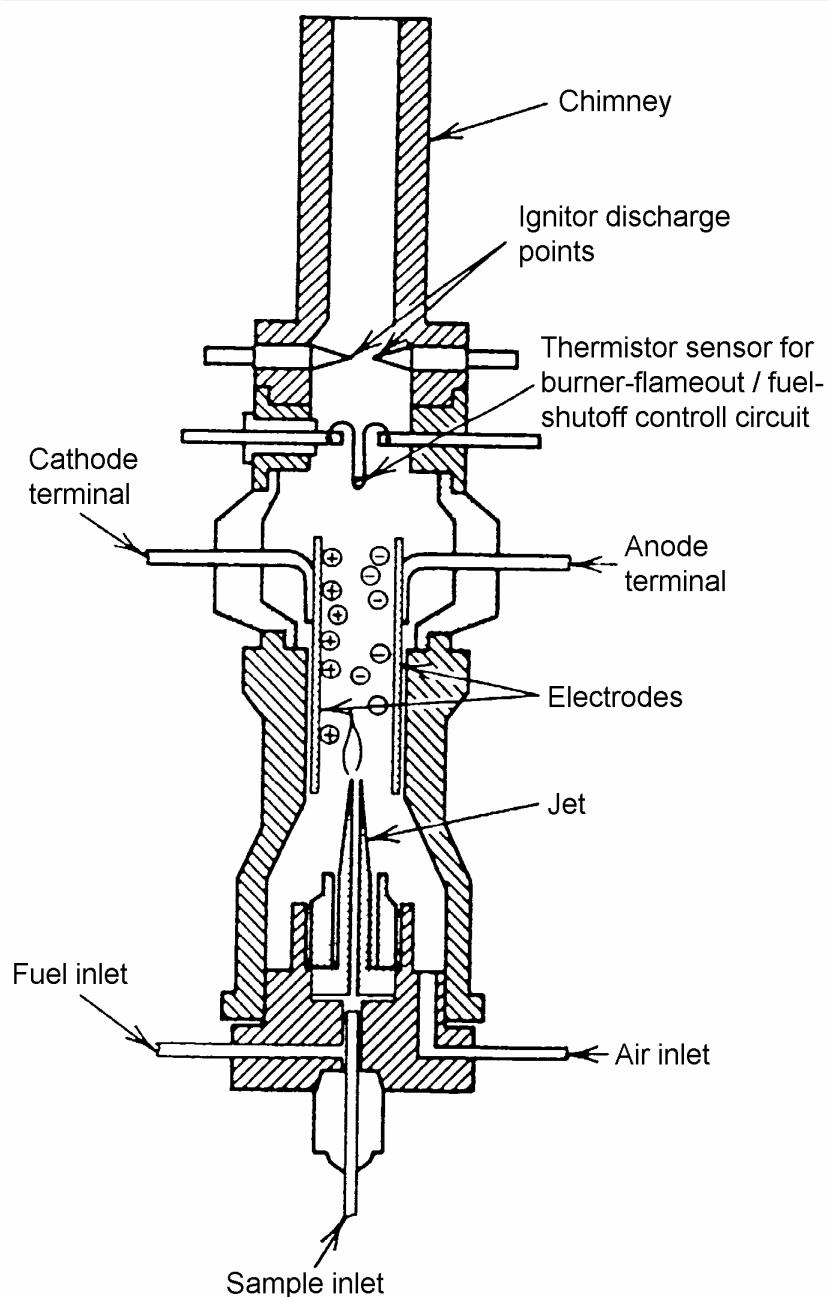


Fig. 12. Sectional view of a burner in a Beckman *flame ionization hydrocarbon detector*.

The magnitude of the current depends slightly on the molecular structure of the hydrocarbon being detected. The instrument counts carbon; and the following concentrations would all read approximately 1 % on the meter:

1.000 %	of	CH <sub>4</sub> ,	methane
0.100 %	of	C <sub>10</sub> H <sub>22</sub> ,	decane
0.132 %	of	C <sub>8</sub> H <sub>16</sub> ,	octane
0.385 %	of	C <sub>2</sub> H <sub>2</sub> ,	acetylene

The flame ionization detector gives no information about the types of hydrocarbons in the sample gas or their average hydrogen to carbon ratio. In recognition of this it is preferred to report measurements as ppmC (parts per million Carbon) rather than as ppm  $\text{CH}_4$  or  $\text{C}_3\text{H}_8$  or  $\text{C}_x\text{H}_y$  equivalent.

Gas chromatography, mass spectrometry, or combinations of the two is used when the appearing hydrocarbon types are studied.

#### Nitric oxide detection by chemiluminescence

Some gases when react with other materials at low temperatures (e.g. atmospheric) emits light. This process is called chemiluminescence. The emitted light is proportional to the concentration of sample constituent, which participate in such reaction.

An ideal model to illustrate the principle on  $\text{NO}_x$  measurement is shown in Fig. 13. The reactor is assumed to be perfectly stirred, that is, homogeneous. To measure nitric oxides we calculate the rate at which photons flow out the window for detection by the photomultiplier.

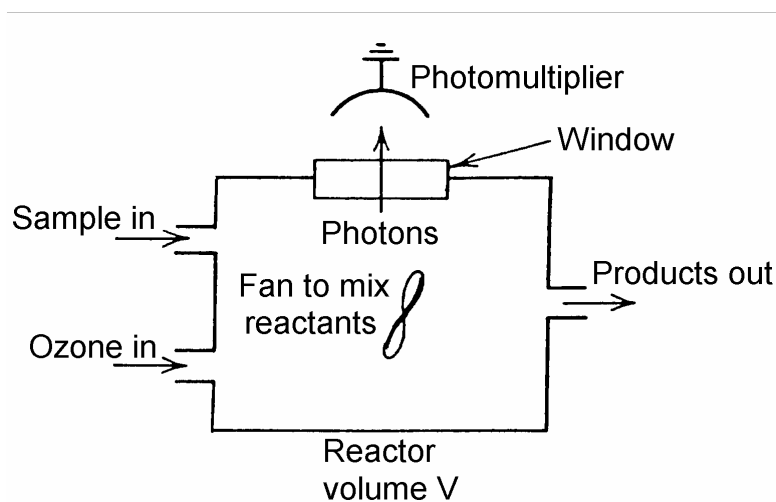


Fig. 13. Schematic layout of the reactor in a chemiluminescent nitric oxide analyser

**PROBLEM SOLVING**

1. A fuel of effective formula  $C_xH_y$  when burned in air yielded an Orsat analysis of 11.5 %  $CO_2$ , 0.7 %  $CO$ , and 2.7 %  $O_2$ . What is  $y/x$  ?

(Answer:  $y/x = 2.649$ )

2. A sample of flue gas had the dry volumetric analysis  $CO_2$ , 12 %;  $O_2$ , 5 %;  $N_2$ , 83%. When the sample of *wet* gas was cooled at 1 bar, its water content just began to condensate at 46 °C. **(a)** Determine the partial pressures of the constituents at 1 bar and 46 °C. **(b)** If the fuel is assumed to consist entirely of C and H, and the water in the flue gas is produced entirely by combustion of H in the fuel, estimate the mass ratio between C and H in the fuel.

$$(p_{CO_2} = 0.10789 \text{ bar} ; p_{O_2} = 0.04495 \text{ bar} ; p_{N_2} = 0.74662 \text{ bar} ; \frac{m_C}{m_H} = 6.37 )$$