AN INTRODUCTION TO COMBUSTION CHAPTER 1

A DEFINITION OF COMBUSTION

Combustion is the process of oxidation of molecules of combustible substances that occurs readily at high temperatures with the release of energy. It is accompanied by that phenomenon which is called "flame" and by the generation of "heat energy".

The combination of carbon with oxygen forms carbon dioxide, a non toxic gas. This process liberates heat and is described as follows:

$$C + O_2 = CO_2 + heat$$

Similarly, hydrogen combines with oxygen and form water vapour (steam) liberating heat. The equation is:

$$2H_2 + O_2 = 2H_2O + heat$$

It is important to observe that the fuel-air ratio is specific and fixed. As a matter of fact the amount of oxygen and fuel in the mixture are in perfect or "stoichiometric" proportions when such substances allow for complete oxidation of the fuel without any residual of oxygen.

With excess fuel or oxygen deficiency there would be a rich mixture and a reducing flame which is long, yellowish and smoky. Such combustion is also called "incomplete combination", since even though some particles are completely oxidized, the remaining ones do not get sufficient oxygen to react completely. The partial or incomplete combustion of carbon is accompanied by the formation of carbon monoxide, a very toxic gas:

$$2C + O_2 = 2CO + heat$$

In this phase the amount of heat released during the process is less than the amount of heat which would be released during a complete combustion. However the incomplete combustion or reducing combustion is sometimes necessary for some special heat industrial processes. However, such conditions must be avoided as far as possible, in all other circumstances.

Viceversa if we add excess oxygen to the mixture, the mixture is said to be "fuel lean" or just "lean" and the combustion is said to be oxidizing. The flame in this case is blue and very short.

As we will explain better later in this chapter, air, which is made up of oxygen and nitrogen, is the oxidizer which is usually used.

If we add "excess air", that is a more than stoichiometric quantity of oxygen, all the nitrogen and part of the oxygen which do not react with the fuel do not take part in the oxidation process.

Obviously they absorb a certain quantity of the heat released during combustion, hence the final heat energy is distributed to a greater volume of gas and the heat level is lower (lower flame temperature).

COMMERCIAL GASEOUS FUELS

These gases are characterized by variables which depend on the quantity of each chemical substance. Here are some fundamental

features of some of the most widespread gases.

(TYPE OF) GAS	MAIN COMPOUNDS	LOWER HEATING VALUE (LHV: kCal/m³)	DENSITY	FLAME PROPAGATION RATE (m/s)
Town gas	CO + H ₂	4.000 ÷ 4.500	0,56	3
Mixed gas	$CO + H_2 + CH_4$ or other	4.500 ÷ 6.000	0,60	1,5
Natural gas	CH ₄	8.500	0,64	0,6
Mixture of propane and air	C ₃ H ₈ + air	6.000	1,20	0,7
Propane	C ₃ H ₈	22.000	1,52	0,7
Butane	C ₄ H ₁₀	28.000	2,00	0,7
Mixture of propane and butane	$C_3 H_8 + C_4 H_{10}$	26.000	1,75	0,7



STOICHIOMETRIC GAS COMBUSTION

For simplicity, we assume throughout this section, that natural gas only contains methane (CH_4). Now the combustion of methane occurs as follows:

$$CH_4 + 20_2 = CO_2 + 2H_2O + heat$$

that is

methane + oxygen = carbon dioxide + water vapour + heat

As both the reactants and products of the reaction are in a gaseous phase, we can say that a m³ of methane (natural gas) needs two m³ of oxygen to complete combustion. It will moreover produce a m³ of carbon dioxide and two m³ of water vapour.

The combination of pure oxygen and methane is only used in particular industrial applications, that is when high flame temperatures are needed, such as in blowpipes. However most industrial combustion applications make use of air, not just pure oxygen, as a comburent. For simplicity, we assume that the simplified composition of air is $20\%\ O_2$ and $80\%\ N_2$. Now as $10\ m^3$ of air per m^3 of methane are necessary, we will have:

$$10 \text{ AIR} = 20_2 + 8N_2$$

Therefore the chemical reaction of methane with air is:

$$CH_4 + 2O_2 + 8N_2 = CO_2 + 2H_2O + 8N_2 + heat$$

In the chemistry of combustion nitrogen molecules are inert hence do not enter the reaction, yet they absorb some of the heat.

In short, to burn a m³ of natural gas completely, 10 m³ of air are necessary.

The combustion of propane, on the other hand, is defined by the following equation:

$$C_3H_8 + 50_2 + 20N_2 = 3CO_2 + 4H_2O + 20N_2 + heat$$

This confirms that one m³ of propane needs 25 m³ of air to complete its combustion.

From the reactions of propane and methane mentioned above, we can deduct that to release 8,500 kCal of heat using 1 m³ of natural gas (whose lower heating value is equal to 8,500 kCal/m³) 10 m³ of air are necessary. Whereas to release 21,000 kCal, using 1 m³ of propane, 25 m³ of air are necessary.

Given these equations, it is clear that both methane and propose follow the same law by which 1.18 Normal volume of combustion air is necessary to liberate 1,000 kCal. To a certain extent we can say that all commercial combustible gases follow this law. We may even say that to some extent it is valid not only for gaseous fuels but also for liquid and solid ones.

QUANTITY OF AIR REQUIRED FOR INDUSTRIAL COMBUSTION

The heat output of burner systems, in particular industrial ones, depends on the quantity of combustion air they manage to mix with gas. Hence the maximum gas capacity in a combustion system is determined by the maximum quantity of air the system can process. Catalogues of burners usually reports the power rating in kCal/h (thousands of calories/hour). At the designing stage and at the moment of choosing which burner or mixer to buy, not only the power rating and gas capacity but also and particularly the quantity of primary and secondary air must be taken into account as well as the capacity of the system to process such quantities.

As the quantity of air necessary for combustion amounts to 1.18 Nm³ per 1,000 kCal produced, no matter what gas is used, all industrial combustion systems complying with this principle, may be considered as "universal" if they are capable of working with any type of gaseous fuels.

In other words, once the quantity of air necessary to obtain good

combustion at some fixed heat potential is known, that system will be able to work with no matter what commercial gaseous fuel to produce the same quantity of heat in perfect combustion conditions. The only change to make when shifting from one fuel to another for equal heat capacities concerns the amount of gas, bearing in mind the calorific capacity of each gas per m³.

For instance, a system having some heat output of 10,000 kCal/h needs 118 Nm³ of air in order to attain perfect combustion. A lower quantity of air would result in a reducing combustion.

If the capacity of fuel was increased in order to deliver 120,000 kCal/h (which is easy to do by increasing the nozzle diameter of the burner) we would have imperfect combustion if we didn't increase the amount of air in the mixture proportionally. The only way to always obtain perfect combustion conditions, when an increase in the heat rating is desired, is to increase the gas and air capacity at the same time.



PRIMARY AIR

Most gas-burner appliances premix some air with fuel gas before it burns. This primary air is less than the stoichiometric air required for complete combustion. The remaining air which is mixed with gas before ignition is called "primary air". The air mixed after ignition is called "secondary air". The quantity of primary air in the mixture is usually expressed as a percentage of the total theoretical air required for combustion; the term referring to all this process is "aeration".

For instance, if a natural-gas burner operates with 80% primary air it means that it is capable of mixing 8 m³ of air per m³ of natural gas before combustion starts. The remaining air, 2 m³ of air per m³ of natural gas, will be added after ignition and is referred to as "secondary air".

Many features relating to flames, depend on the amount of primary air a combustion system can process. The less the primary air, the softer and longer the flame.

THE MECHANISM OF COMBUSTION

The chemical equations relating to natural gas mentioned above in this chapter quantify the air and natural gas necessary for theoretical combustion as well as the amount of the final products of such combustion. However these equations do not explain the physical and chemical aspects of combustion.

Concerning the nature of the gaseous state, it is known that the molecules of a gas are in rapid motion, or "thermally agitated" and collide frequently with each other. The higher the temperature the faster the motion of the molecules; viceversa the lower the temperature the slower the motion.

In a perfect mixture of oxygen and natural gas (methane) there are always 2 oxygen molecules per methane molecule. Methane contains 4 hydrogen atoms that are linked by one chemical bond to the carbon atom. The oxygen molecules contain 2 oxygen atoms linked one to the other by two bonds.

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In order to start combustion, it is necessary that the hydrogen atoms split from the carbon atoms and that oxygen breaks the bonds which link them together so that they are free to react with carbon and hydrogen

The splitting of the hydrogen, carbon and oxygen atoms is the result of the collision of the molecules with each other. At ordinary temperatures the collision is so weak that atoms are not able to break the bonds.

At high temperatures, collisions involving high energy become more frequent, and at 650 °C this lead to breakup and chemical combination of the colliding molecules.

Methane oxidation is impossible below 650 °C, on the other hand at

650° C and over the free carbon and hydrogen atoms start looking for oxygen: combustion has just started. The chemical reaction of oxidation of the hydrogen and carbon atoms results in the physical phenomenon called flame and heat. The latter is often used in thermal processes.

Combustion occus generally by reaction chains. For instance, at 650 °C, a high-energy collision breaks up a molecule into atoms or "free radicals"; such a molecular fragment reacts with a molecule of fuel gas, which thereby becomes capable of reacting with an oxygen molecule; in the latter process, an atom or free radical is again released, thus continuing the chain. Chains are broken when two atoms combine to form a stable bond. The speed at which this chain reaction takes place determines the "flame propagation rate" of a mixture. The amount of heat liberated during the combustion of a mixture of pure oxygen and natural gas is sufficient to increase the flame temperature to some 2,850 °C.

As we have already said, in industrial combustion applications, apart from very particular circumstances, oxygen is taken from the air of the atmosphere.

During the combustion reaction, the nitrogen in the air absorbs a certain quantity of the heat which has been released. This phenomenon obviously results in a slowed-down chain reaction, hence the transfer of heat from one molecule to the other is slowed-down and the flame propagation rate is also slowed-down. Nitrogen acts as a diluent of the combustion reaction.

The maximum theoretical temperature which can be obtained in the flame produced by methane combustion with air amounts to some 1,930 °C; in reality the maximum temperature which can be reached in a methane-air industrial oven is about 1,800 °C. The heat radiated by the flame as well as other losses prevent the temperature from reaching the maximum theoretical temperature.

Higher combustion temperatures may be reached by mixing oxygen to combustion air. This results in proportionally reduced quantities of



nitrogen in the reaction and therefore in a weaker diluting effect. Higher temperatures may also be obtained by preheating combustion air or air and fuel gas at the same time so as to save a certain amount of calorific energy which is necessary to raise the temperature of the molecules to the ignition point. For instance, by preheating a mixture of air and natural gas to 260°C, an increase in the flame temperature of some 100 °C may be obtained.

INCOMPLETE COMBUSTION - FLAMELOSS

Scientific research on the mechanisms of combustion have shown that the chemical process of combustion go through intermediate products before producing the final products of maximum oxidation, which are carbon dioxide and water vapour. The main intermediate products of combustion being carbon monoxide and aldehydes.

During the chain reaction, started by the colliding molecules, allowing for the oxidation of atoms with the subsequent heat release, these intermediate products are formed. The latter are readily transformed through oxidation as they get in contact with oxygen in carbon dioxide and water vapour molecules.

Once started, the combustion reaction must go on at a temperature higher than the minimum ignition temperature. If at any moment, in the flame mass, the burning mixture is cooled down to a level lower than the minimum ignition temperature, combustion stops and the flame extinauishes.

When plunging any cooling or refrigerating medium in the mixture during combustion, this medium absorbs heat and subtracts it to the combustion process. If the cooling medium absorbs enough heat to avoid the molecules of the compounds in the reaction in contact to reach the ignition temperature, combustion either stops altogether or stops in those areas where it touches the cooling medium. This would take place even if the fuel and comburent were in a stoichiometric proportion.

In practice the hazard of incomplete combustion or flameloss only exists in low-temperature industrial applications, as for instance in combustion systems working with recirculation air as the latter may act as a cooling medium. Long flames, which are not protected and hence subject to important cold air current may be disturbed by the current particularly on the outer surface. Though in the inner part of the flame, combustion pursues at a temperature ranging from 1,000 to 1,700 °C, it may happen that the mixture licking the outer cold air, blows-by though still unburned.

Incomplete combustion due to a cooling medium may stop the reaction of the fuel with the comburent at the intermediate stages. In these conditions it is easy, for some particularly sensitive people to smell pungent aldehydes.

Should this happen it is advisable to check the system, look for the causes and readily solve the problem.

FLAME PROPAGATION RATE

Mixtures operating with 100% primary air, that is needing no additional air to complete combustion, even before reaching the point where combustion starts, have the maximum flame propagation rate therefore for equal gas capacity they produce the shortest flames. Rich mixtures, which on the contrary need some secondary air to complete combustion, will produce longer flames as secondary air

needs some time to mix with fuel gas.

The flame propagation rate is proportional to the quantity of premixed air.

In some particular circumstances the flame propagation rate incrases with an increase in the speed of air-gas mixing.

