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COMBUSTION CHARACTERISTICS

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COMBUSTION CHARACTERISTICS (INTRODUCTION)

There is much more to combustion than a fuel in air and an ignition source. To better appreciate the wide range of involved phenomena, a description of combustion basics (combustion types and processes), and combustion applications (combustor types and systems), is presented here, before a more rigorous treatment of the thermodynamics, kinetics and metrology of combustion.

COMBUSTION FUNDAMENTALS (WHAT IT IS)

Everyone knows from infancy what a fire is; humans have always felt a mixture of fear and magical appeal for fire. Combustion is burning, a self-propagating oxidative chemical reaction producing light, heat, smoke and gases in a flame front. Combustion is a process and fire is the actual outcome. What does it mean in more detail?

- Combustion means burning (lat. *cum urere-ustus* = burn), e.g. burning wood in air, natural gas in air (or $\text{CH}_4/\text{O}_2/\text{N}_2$ mixtures in general), hydrogen with oxygen (H_2/O_2 in gaseous or liquid forms, and not only H_2 in O_2 , but O_2 in H_2), and more bizarre burnings, such as sodium with chlorine ($\text{Na(s)}/\text{Cl}_2(\text{g})$), aluminium powder with water, magnesium powder with carbon dioxide, nitrocellulose (cellulose is $-(\text{C}_6\text{H}_{10}\text{O}_5)_n-$ with $n=300..2000$) within any medium, etc. But the meaning of combustion is usually restricted to easily flammable substances (typical fuels) in ambient air. [Fuels and oxidisers](#) are presented aside.

- Self-propagating, means that, once it ignites, it goes on, sustained by the high temperatures and radicals (active species) produced, until either the fuel or the oxidiser practically runs out, or an extinguishing agent is applied that prevents fuel-and-air mixing, or cools the system well below autoignition, or scavenges active species. Notice the two sequential steps in combustion: first there is an endothermic process of ignition, followed by a much more powerful exothermic process of runaway oxidation that propagates the process. Any exothermic adiabatic system will show a thermal runaway at some high enough temperature (autoignition), but for real non-adiabatic systems, ignition criteria are governed by an interplay between heat-release rate and heat-loss rate. Materials are termed non-combustible if they cannot be ignited below 1000 K.

Combustion propagation is usually a slow process; very slow indeed for solid and liquid fuels: <0.1 mm/s for a candle flame (that were used as clocks to measure hours), ~ 1 cm/s for flames spreading on solid fuels, usually <0.5 m/s for premixed fuel-and-air gases burning at rest (although it may be raised to 100 m/s in high-turbulent flows, and may reach >1000 m/s in detonations). However, a common feeling and fear is that combustion is explosive, because the pressure-rise in confined spaces may give rise to violent mechanical explosions (brick walls are not pressure vessels).

According to the mechanism for propagation, several types of combustion processes may be distinguished:

- Thermal free-flame gaseous combustion: the usual case for combustion, e.g. in a candle, a lighter, a bunsen, an internal combustion engine (reciprocating or turbine), a furnace, a boiler, etc.
 - Thermal trapped-flame combustion in porous refractory media: a new combustion procedure derived from the common one above-mentioned, to substantially increase combustion intensity and stability, but problems of refractory materials exist.
 - Smouldering (or Thermal non-flame combustion of porous media): the slow burning without flame of porous combustible matter, e.g. cigarettes, wood or coal embers, etc. It has little engineering use, but great safety interest because uncontrolled fires usually start by smouldering.
 - Catalytic combustion: active species, instead of temperature, may propagate the combustion process, usually without flaming: e.g. room-temperature reaction of hydrogen and oxygen in a platinum surface (it may flame if a large contact area exists, as in a porous catalyst that releases so much heat as to ignite the rest).
 - Detonating combustion: when the combustion process is coupled to a high-pressure shock wave, travelling at supersonic speed.
- Oxidative chemical reaction. Combustion is an electron-exchange reaction (a 'redox' one), not a simple electron-cloud distortion as in proton-exchange (acid-base) reaction. The fuel atoms supply electrons and get oxidised, whereas the oxidiser atoms get the electrons (get reduced).
 - Light, heat, smoke and gases in a flame front. Combustion results in a large temperature increase in the products, typically from 300 K to 2500 K, causing them to be in the gas state (except for

soot and more rare refractory particles) and establishing a radiation imbalance in the infrared and visible ranges. Light emission in flames only approaches blackbody radiation if there are solid particles, such as soot found in non-premixed flames (e.g. yellow bunsen). For premixed flames, light is by chemiluminescence in special spectral bands, and very dim in intensity (e.g. blue bunsen).

It is the visible light of non-premixed flames that has been traditionally identified with combustion (it is the standard symbol for fire). In fact, it might help to think of the flame as an invisible, very hot, burning interface, made visible by non-burning incandescent substances passing by or being created, for instance soot particles in non-premixed flames (their sublimation temperature is around $T_{\text{subl}}=3900$ K), sodium ions in salt-seeded flames (above the salt boiling point $T_b=1690$ K), or calcium oxide in limelight ($T_b=3100$ K). The latter was used in the 19th c. in theatres as the brightest, most natural-colour artificial light available, being produced by placing a block of lime against a hydrogen/oxygen jet flame (practically invisible in spite of its 4000 K temperature; lime melts at 2850 K). The Sun also gives light and heat (at a temperature of 5800 K in its surface) but by nuclear fusion reactions in the interior (where the temperature may reach 10^7 K) and not by chemical combustion.

What it is not

Combustion vs. explosions

Combustion means burning and explosion means bursting, i.e. combustion is a relatively slow chemical process yielding light and heat, whereas explosion is a sudden mechanical process causing rupture and noise, due to great pressure forces that may be originated chemically (e.g. from a confined combustion), thermally (as in boilers, even electrically heated), mechanically (as in a balloon or any other gas-pressurised vessel), nuclearly, etc. Detonation, the [supersonic combustion](#) taking place under some circumstances in premixed fuel/oxidiser gaseous mixtures and many explosives, is studied aside.

Combustion vs. fuel cells

Fuel cells are electrochemical generators, like batteries but with continuous fuel-and-oxidiser supply. Reactions inside a fuel cell, although globally equivalent to combustion, are not properly combustion because they do not self-propagate (reaction in a fuel cell stops as soon as the electrical load is switched off, it shows no thermal-runaway). A non-premixed burner (e.g. a lighter) may be thought of as controllable as a fuel cell (as soon as the fuel injection stops, combustion ceases), but it does not simply start over if reopened. A controllable-area catalytic combustor, however, more closely resembles a fuel cell: no need of igniter, simple reaction control, and for small active areas there is no runaway (a big difference is that fuel cell directly generates electricity and the catalytic combustor just heat).

The igniter in a combustor (a spark or a hot wire) and the electrical connector in a fuel cell, act as catalysts that provide a gateway for the reaction; in both cases there is an electron-transfer reaction (redox reaction), the main difference being that the transfer of electrons from fuel to oxidiser is restricted in a fuel cell by electrode-interface-area and electrolyte-ion-diffusion, with the external electrical connector required all the time, whereas in normal combustion the electrons transfer is only limited by diffusion in the bulk, and the igniter is only needed to start the process. Entropy generation, positive in both cases, Combustion characteristics

tends to zero in a fuel cell at very low intensities, but it is always above a certain finite value in combustion.

Combustion vs. oxidation

Combustion is a self-propagating oxidative chemical reaction characterised by a thermal runaway; i.e. it is a quick exothermal oxidation. The same system may undergo slow oxidation or combustion, with the same initial and final states, but with different paths (e.g. paper turns yellow (and brittle) with the years because of slow oxidation, but may burn in seconds). Notice also that oxidation may be exothermic or endothermic, whereas combustion is always very exothermic.

THERMAL FREE-FLAME GASEOUS COMBUSTION

This is the usual case for combustion, that self-propagates as a result of the high temperature (1500..3500 K) developed after initial ignition (e.g. by a spark), due to a more-or-less adiabatic conversion of chemical-bond energy to internal-thermal energy within a reacting gas mixture (for condensed fuels, the latent heats for vaporisation and possibly decomposition has to be subtracted).

According to the initial state of mixing of fuel and air, combustion process can be classified in the limit as premixed and non-premixed (real processes are in between), with a corresponding premixed and non-premixed flame. In premixed combustion the unburnt gas is already a perfect mixture of fuel and air, and the burning or flame-propagation speed is only limited by the chemical kinetics of the reactions involved and heat diffusion forward, whereas in non-premixed combustion there is not a characteristic burning or flame-propagation speed, the speed being fixed by the flow-rates of fuel and oxidiser that must approach the flame by diffusion from each side.

Steady free flames demand an astonishing fine balance for heat and mass flows (e.g. think why a candle flame sits at a precise distance up the wick). If adiabaticity of the initial ignition region is prevented by nearby heat sinks, as a cold solid wall, this kind of 'thermal' combustion cannot propagate (safety lamps and quenching grids are based on this fact); e.g. for premixed methane/air stoichiometric mixtures, thermal free-flame combustion cannot propagate inside a metal tube of less than 2 mm.

Thermal flames are almost always established in a gas phase: in a fuel/air gas mixture or in the fuel vapours diffusing in air, from liquid or solid fuels. Only refractory fuels like coal to some extent, tantalum or zirconium, burn at the solid surface; iron and titanium, having intermediate melting points for both the metals and the oxides, burn at the surface of a molten mixture of the metal and its oxide, whereas aluminium and magnesium, which have low boiling points, vaporize and then burn in the gas phase.

The presence of condense matter is always a handicap (all condensed fuels burn worse than their vapours), and this fact is used in fire-fighting. However, flames may be sustained inside liquids in a suitable gas envelop. In order to maintain a steady underwater flame (e.g. a hydrogen or acetylene welding torch), it is necessary to form a stable bubble, usually achieved with an additional compressed-air jet-stream introduced around the tip of the torch, since the exhaust gases cannot maintain it by themselves (a great deal of skill is required of divers who perform this kind of work).

Thermal free-flame combustion cannot propagate if the air/fuel ratio lies outside of the lower and upper flammability limits at ambient conditions: e.g. 5% and 15% of fuel by volume of mixture for methane/air flames, respectively, although increasing temperature widens this range. Neither can flames propagate also at very low pressures (a fire safety rescue in spacecraft).

THERMAL TRAPPED-FLAME COMBUSTION IN POROUS MEDIA

Flames cannot propagate through small holes in a solid (this is how Davy's safety lamp work), unless the solid is hot enough (say >1000 K), what can be achieved by holding a lit free flame close to the solid for some time. For instance, if a premixed methane/air stream is forced through a finite porous medium (usually solid, but also fluidised), and ignited at the exit, the free-flame formed may travel upstream or downstream according to the flow speed. If the injected gas speed matches the deflagration speed, the flame sits steadily at the mouth and, after the porous end gets hot, slowly decreasing gas injection speed allows the flame to go backwards and penetrate the porous media, which is being heated by the slowly moving flame front. The process is also known as filtration combustion.

Notice that the flame-front temperature is lower than the adiabatic value when the front moves backwards, but, if the gas injection speed is increased to force the flame to travel downstream, then its temperature is above the adiabatic value (it is moving into an already hot solid).

Presently only Al_2O_3 and ZrO_2 can work above 2000 K, SiC and FeCrAl-alloys being used below 2000 K with the advantage that they have larger thermal conductivities and mechanical resistance. In spite of this basic materials difficulty, porous-medium burners have several advantages:

- Less NO_x emissions because of lower temperatures.
- More compact because the deflagration speed increases from 0.5 m/s to 4 m/s (they reach 3000 kW/m^2 instead of the 300 kW/m^2 of normal burners).
- Wider range of ignitable compositions (lower limit decreases from 5% to 4% in methane/air flames, increasing the air ratio from $\lambda=1.9$ to $\lambda=2.2$, allowing for leaner mixtures to be burnt, yielding lower emissions).
- Wider power-modulation range (0.1 to 1 times full load, against 0.5 to 1 for normal burners, so that start/stop cycles and accumulators are avoided). Porous media combustion was developed aiming to stabilise premixed flames near their lower stability limit.

SMOULDERING (THERMAL NON-FLAME COMBUSTION OF POROUS MEDIA)

Before, combustion 'in' a porous-media was considered; now combustion 'of' a porous-media-fuel is analysed. Some porous (solid) fuels may sustain a self-propagating combustion inside their matrix, i.e. an heterogeneous reaction, at a very low rate and low temperature, taking the oxidiser from the ambient through its pores, with little or no visible flame, but with change of external texture (which chars) and smoke emission (sometimes very toxic).

A typical smouldering process takes place in the tip of a lighted cigarette. The porous fuel is inside a porous cylindrical envelop (of paper in a cigarette, or a full tobacco leaf in a cigar) containing crashed dried tobacco leaves (they were smoked or chewed by American Indians since ancient times because of the euphoric action of nicotine). Once the cigarette lighted, if left in still air without drawing, a dim

Combustion characteristics

burning happens with maximum temperatures of some 850 ± 50 K at the centre and some 650 ± 50 K at the periphery. During drawing, however, those values go up to 1000 ± 50 K and 850 ± 50 K, respectively.

A big fire-safety problem is that, the burning taking place in the insides, smouldering can progress undetected for long periods of time (smoke detectors are used, but diffusion is very inefficient. Thus, under certain circumstances, smouldering may undergo a sudden transition to flaming; that is why some forced convection of cabin-air and avionics-air is always procured in spacecrafts, where buoyancy forces are absent, to help an early detection.

CATALYTIC COMBUSTION

Even in the close proximity of cold solids, combustion may be sustained if there is some catalytic substance that lowers the activation energy and sustains the combustion process at low temperature at the porous surface; e.g. H_2/air react over Pt at room temperature, CH_4/air over Pt requires 350°C . The most developed catalytic combustor uses $\text{C}_4\text{H}_{10}/\text{air}$ over Pt-coated ceramic matrix at 500°C . Low-temperature catalytic combustors work in the 300..600 K range, and high-temperature catalytic combustors work in the 700..1400 K. They may work with premixed flows and with a non-premixed fuel-flow and ambient air.

The advantage of power modulation, widening of ignition limits and less emissions, are maintained or increases here (<1 ppm for NO_x and CO, due to very low temperatures involved), but not the higher burning rate (that was due to thermal conduction along the hot solid matrix, and thus only 600 kW/m^2 are achieved instead of the 3000 kW/m^2 of thermal porous-medium burners. At intermediate temperatures, an hybrid regime of catalytic-assisted thermal combustion may be developed, where both heterogeneous and homogeneous reactions take place, an interesting trade-off solution when the catalyst is too expensive and very little can be used (in full catalytic mode, if there is insufficient catalyst, part of the fuel slips to the exhaust (increasing pollution and expense), or even the whole fuel if the catalyst cools down and deactivates. The influence of the flow rates is important; for instance, if a thin porous solid is doped with a catalyst and a premixed methane/air stream is forced through, an exothermic oxidation of the fuel takes place if the temperature is >600 K, releasing much of the lower heating value, what causes the matrix to reach some 1500 K at the outer surface (the hotter) in a flameless regime with a power of up to 500 kW/m^2 ; but if more gases are fed, small flames detach from the outer surface and at about 1000 kW/m^2 a blue flame at some 1900 K forms immediately close to the outer surface, that only reaches now some 600 K.

DETONATING COMBUSTION

Supersonic combustion, called detonation, is realised when combustion gets coupled to a shock wave travelling at supersonic speed. Detonating combustion is considered under Explosives in [Pyrotechnics](#), and under Supersonic combustion in [/Combustion kinetics](#).

COMBUSTION APPLICATIONS (WHAT IT IS FOR)

Combustion is an old technology to humankind, only second to simple mechanical tools made of wood, bone and stone. Is it just then a subject of historical interest? For instance, from pre-historic times (some

500 000 years ago, at least) to the end of XIX c. the only lighting method was combustion, but today only electrical lamps are used, so, why spending effort on incandescent lighting?

We want to devote an effort to understand combustion processes for several reasons:

1. To understand it (i.e. for its own sake, the general interest to broaden our knowledge of the world).
2. To minimise the risks and damages of controlled combustion and uncontrolled fires (safe fire handling).
3. To advance the efficient use of fossil fuels (quickly exhausted) to satisfy our needs (e.g. transportation propulsion, electricity generation).
4. To alleviate the problems associated to combustion emissions.

Combustion always gives off heat and gases, most of the times light, and sometimes smoke (a nuisance in non-premixed flames, and the major personal danger in fires). Combustion is the major energy release mechanism in the Earth (it is gravitational dissipation in jovian moons). Why? Because the Earth atmosphere is plenty of free-molecular oxygen (50%wt of the whole ecosphere is oxygen, but mostly in compounds) and Earth ecosphere is plenty of fuel (all living matter plus fossil fuels). Why? It is nearly a miracle because at the start of the Earth ages, $4.5 \cdot 10^9$ yr ago, there was no O_2 but some H_2O that generated a small amount of O_2 by solar-radiation hydrolysis, part of which was transformed to UV-shield O_3 by solar radiation and thus allowed the start and survival of primitive plants. Plant photosynthesis has generated all O_2 in the atmosphere and all living (and fossil) fuels on Earth. Combustion (controlled and uncontrolled) releases an average of $10 \cdot 10^{12}$ W in the globe, as compared to $0.5 \cdot 10^{12}$ W due to nuclear disintegration (controlled and uncontrolled), $3 \cdot 10^{12}$ W due to geothermal heat flux and $120\,000 \cdot 10^{12}$ W due to the solar absorption.

Combustion is key to humankind today as in the past and the foreseeable future; it is worldwide the major energy-release process (nearly 90% of the world primary energy is to be burnt), it is the major environmental-pollution process, and fire is one of the most feared natural disasters. Roman Emperor Augustus established a corps of fire-fighting watchmen already in 24 b.C.; their fire-fighting techniques are still applied: removing heat by throwing water with a bucket passed from hand to hand, removing the fuel by cutting it aside with an axe (or, at a much later times, by providing firebreaks), and opening doors and windows in enclosures to get rid of smoke and let fresh-air in for people sake (unfortunately feeding the combustion process, too).

Even nowadays 88% of world commercial energy consumption (i.e. excluding photosynthesis and uncontrolled fires) is by combustion (plus a 5% hydraulic and a 7% nuclear fission, roughly). This combustion-released energy (as any energy) is used today for:

- Heating. Internal chemical energy is first released to internal thermal energy (high temperature), and then heat transfer to the load takes place.
- Propulsion and electricity generation. Mainly by means of a heat engine with a working fluid that may be an independent one (e.g. steam), or directly the combustion products.
- Refrigeration. By an absorption refrigerator driven directly by the combustion products or through an intermediate fluid (e.g. steam).

- Chemical transformations. Mainly as a heating application, but sometimes directly for reduction, oxidation, incineration, reforming, etc.
- Light emission was a major application of combustion up to the XIX c., but nowadays it is a rarity: candles, rescue signals, fireworks.

There are other unusual applications of combustion, as smoke generation for visualization, gas generation for fuel-tank inertisation, aromatherapy, etc. [Explosives](#) applications are considered aside.

HEATING

Heating for space conditioning or for materials processing (domestic and industrial) has always been the basic combustion application. Energy efficiency in heating is usually measured as the fraction of the lower heating value of the fuel that is fed to the system to be heated (the rest is lost by the flue), and it is close to 1 (that is not a limit: heat pumps can give more).

A special heating application is the cutting of materials. Thick metal plates can easily be cut with a normal gasoline, propane or oxy-acetylene torch, with additional oxygen to burn the metal (that is a fuel itself; hint: think of $M+O_2=MO_2$, as for carbon). For cutting or piercing thick ceramic objects, a thermal lance is used, in which, an iron tube act as the fuel that burns (once ignited) with oxygen being supplied through it (sometimes in the cryogenic liquid state). A small 5 mm-diameter tube, 0.5 m long, may burn for one minute consuming some $50 \cdot 10^{-3}$ kg of oxygen, producing a >5000 K flame that would pierce a 150 mm-thick steel slab in less than 10 s (a 0.5 m deep hole can be pierced in stone or concrete in a few minutes, anywhere: in the air, under water, or within mud and slurries).

PROPULSION AND ELECTRICITY

Motion and electricity generation, by means of heat engines (vapour and gas cycles), constitutes the foundations of Thermodynamics. For electricity generation, energy efficiency is measured by the ratio of electrical energy delivered divided by the lower heating value of the fuel (it typically ranges from 0.2 to 0.5), or by the specific fuel consumption (of the order of 60 g/MJ or 200 g/kWh), and it could be similarly done for mechanical power, although for cars it is usually done in litres of fuel consumed per 100 km travelled (or in miles per gallon in the USA; the change is $x \text{ [mph]}=235/x \text{ [L/100 km]}$).

ABSORPTION REFRIGERATION

Absorption-refrigeration machines use heat (usually from steam or from a fuel burning) to separate the working vapour from a high-pressure liquid mixture. The working vapour condenses in a heat exchanger with the ambient, and is flashed through a restriction to a low-pressure heat exchanger where the cooling effect is produced, exiting into a liquid absorber that is pumped and closes the loop. Energy efficiency is usually measured as the amount of cooling divided by the amount of fuel or steam consumed (in vapour-compression refrigeration, energy efficiency is measured by the ratio of cooling energy to electrical or mechanical energy input).

CHEMICAL TRANSFORMATIONS

Some materials processing, e.g. mineral reduction, cooking, distillation, require an exergy supply (other materials processes are used as an exergy source, as combustion); incineration may have positive or

negative heat balance, depending on the materials. In the typical case of energy consumption, energy efficiency is usually measured as the amount of material processed divided by the amount of fuel consumed.

COMBUSTION SYSTEM TYPES (HOW IT IS DONE)

According to the steadiness of the control frontier (real or imaginary), and to how the propagation is maintained, one may distinguish several type of combustors, traditionally grouped in steady combustion chambers and unsteady combustors.

STEADY COMBUSTION CHAMBERS

Steady state combustion takes place in industrial heaters, furnaces, boilers, steam turbine boilers, gas turbines, and domestic appliances: from the cooking range to the gas lighter. Steady refers to the average process, but it does not mean that the process is locally steady; most practical systems operate in a highly turbulent regime. The combustion process may approach the non-premixed flame model or the premixed flame model, according to how much fuel-and-air mixing exists before burning. Walls must be cooled to avoid materials problems at the high temperatures involved (>2000 K), and, most of the times, excess air is used to cool the main burnt flow, that is nearly stoichiometric (see Fig. 1a).

Recently, partial recirculation of exhaust gases is being applied (instead of the secondary air in Fig. 1a) for emission reduction, heat recovery, autoignition and flame stabilisation. Exhaust gas recirculation (EGR) helps to keep a high uniform temperature inside the combustor, but lower than the hottest region in normal flames; e.g. a maximum $T \approx 1800$ K with maximum spatial deviations of $\Delta T \approx 100$ K, entering the air/EGR mixture at some 1500 K with as low as 2% O_2 and producing a wide dim green flame, whereas, in normal combustion, air enters at 300 K with 21% O_2 , producing a bright and long yellow flame with maximum temperature $T \approx 2500$ K with maximum spatial deviations of $\Delta T \approx 1000$ K.

A modern home boiler (Fig. 1b) is a friendly, efficient and environmentally-clean combustion appliance; it is permanently ready (safe, reliable, no surveillance, no servicing, 20 years life), provides some 20 kW of space heating or hot water for sanitary use, is fed by natural gas that burns with 3% excess air, extracting 94% of the maximum heating value (105% in terms of its LHV, due to exhaust condensation), is small and silent, and only produces 80 mg/m^3 of NO_x as major pollution (besides the CO_2 inherent to the fuel carbon content).

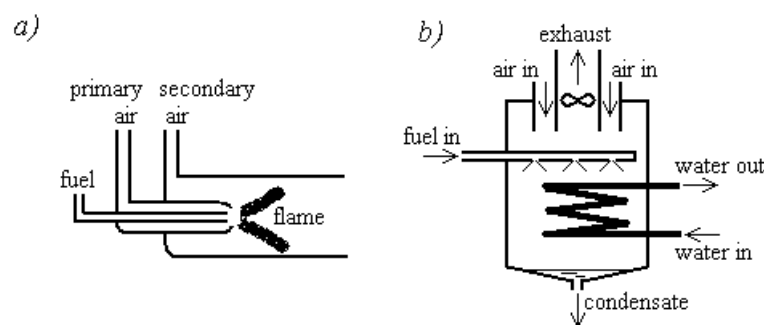


Fig. 1. Steady combustion chamber layouts: a) industrial burner, b) domestic water heater.

Solid fuels are no longer burnt in chunks over a grate, but gasified (pyrolysed), pulverised (fine dust) or fluidised (coarse granulate made to levitate by air entrainment). Dry (<15% water) coal powder (1 mm size) can be burnt in cyclonic or screw burners, although it is expensive and only worth for >3 MW.

UNSTEADY COMBUSTION CHAMBERS

Unsteady combustion chambers are used in reciprocating internal combustion engines (ICE); also in the (non-reciprocating) Wankel engine, not further mentioned here because of lack of use. The combustion process may approach the non-premixed flame model (for the major part of the fuel burning in a diesel engine), or the premixed flame model (for the spark-ignition engine and the initial stage for compression-ignition engines). The period of burning and fluids renovation is so short, that the thermal inertia of the wall materials makes higher peak temperatures allowable in the gas, contrary to steady combustors.

The two basic ICE realisations are the spark ignition engine (SI, gasoline, or Otto) and the compression ignition engine (CI, diesel oil, or Diesel). The normal working for a SI-engine is with a premixture of fuel and air at the stoichiometric ratio, tuning the output power by essentially chocking the entrance duct, whereas for a CI-engine non-premixed fuel is added to highly-compressed air. SI-fuels must have high volatilities (or be gaseous) for quick mixing, and have a high resistance to autoignition, to avoid knocking. CI-fuels must have a low autoignition temperature and short delay.

The best ICE are direct injection (DI) exhaust gas recirculation (EGR) engines, both of Diesel and of Otto type, the latter with stratified mixture (by injection control) and exhaust catalytic converter. Typical air/fuel relative ratios are $\lambda=0.9..1.05$ for Otto engines, $\lambda=1.3..1.8$ for normal Diesel engines, and $\lambda=1.6..2.1$ for large (>500 kW) slow (<200 rpm) marine Diesel engines.

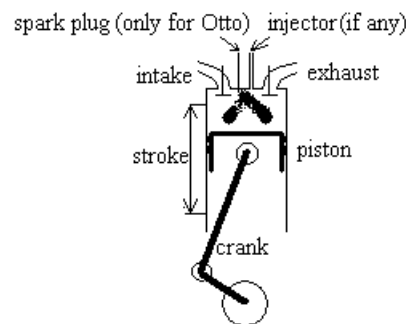


Fig. 2. Unsteady combustion chamber in an internal combustion engine.

A modern direct-injection turbo-charging diesel-engine for a small family-car (like in Audi A2 1.2 TDI, or VW Lupo 3L TDI) is a friendly commodity: it is safe, easy to start, reliable (2 years typical maintenance-free, 10 years typical mean-time between failure, 20 years life), providing some 50 kW of mechanical power with its 1200 cm³ total piston displacement and 18:1 compression ratio, it injects the fuel directly to its three cylinders in line at more than 100 MPa when the compressed air is at some 6 MPa and 700 °C, extracting some 50% of the maximum work-value of the fuel (some 30% energy efficiency in terms of its LHV), it is small and not too noisy and shaky, producing less than 0.3 g/km of NO_x as major pollution (and <0.1 g/km of CO, and <0.02 g/km particulate matter, besides the CO₂ inherent to the fuel, yielding some 100 gCO₂/km), and is able to power a 5-seat car at 170 km/h consuming 3 litres every 100

km (at 90 km/h on good roads). Presently, however, EU and Japan cars are typically 2-litre, 4-cylinder, 80-kW engines, whereas USA cars are typically 4-litre, 6-cylinder, >100 kW-engines.

It seems that both Otto and Diesel engines are converging towards an hybrid, the new Homogeneous Charge Compression Ignition engine (HCCI), where fuel injection during the compression stroke creates a very lean mixture that auto-ignites by premixed compression near the top dead centre, producing a better combustion for a steady regime (it is difficult to control the time of ignition if unsteady): less soot and lower NO_x emissions (lower temperatures) than a diesel engine, and higher efficiency than an Otto engine (but unburnt emissions in between).

CATALYTIC COMBUSTORS

Catalytic combustors are porous catalytic solids inside which a low-temperature combustion takes place. They are not so much developed as the simple thermal combustors above-mentioned (steady and unsteady). They have the advantage of very complete oxidation (low emissions) and low-temperature work, but they are expensive and bulky. They may be used for:

- Catalytic burners, where heat is generated by burning a main fuel (C₄H₁₀, CH₄, H₂) in a catalytic porous media. They are mainly used as radiant catalytic heaters for stoves and open-air industrial heating (e.g. to cure the epoxy used to join pipes in gasoducts and pipelines, to dry wood and other biomass).
- Catalytic-assisted burners, where very lean mixture may be burnt at moderate temperatures, avoiding the formation of NO_x. They are being introduced in gas-turbine engines and plants.
- Catalytic converters, where emissions are remediated without interest in heat generation (e.g. CO and VOC in car exhausts are completely oxidised). This is the most developed application; most modern cars have a catalytic converter in the exhaust pipe (see Three-way catalytic converter).

Although simple stagnation flows over a catalytic plate are studied in the lab, practical systems consist of monolithic honeycombs or granular material (porous media of 1 mm typical porous size), because of the surface effect on heterogeneous reactions. The combustion catalyst per excellence is a platinum doped refractory matrix.

Catalysts may work at room temperature (as in Pt for H₂/O₂), but most usually they require some initial heating (as in Pt for CH₄/air), achieved electrically (from the mains, or with a battery), by a conventional pilot flame, or even by a room-temperature catalytic combustor (as in hydrogen-assisted natural-gas catalytic combustor). The element preheats the catalyst bed to some 400 K, the temperature at which the catalytic pad will sustain a chemical reaction with the fuel and ambient air, and the fuel supply is regulated to operate steadily at some 700 K.

POROUS BURNERS

Porous burners are porous non-catalytic solids inside which a high-temperature combustion takes place with small flames trapped in the pores. They are in the development stage, showing promise of very high combustion intensities (3000 kW/m² of cross-section) and low emissions, because of increase heat transfer and flame stability. They may work with a premixed flow (fuel and air been forced through one end), or, more rarely, with a non-premixed fuel flow that meets a back-diffusing air flow at the exit.

Premixed porous burners consist of two sequential stages: the premix fuel/air stream first enters a fine-pore hot solid matrix (below the flame quenching size, for safety), where it is heated until it enters the second larger-pore hottest solid matrix, where alveolar flames stabilise themselves for a wide range of flow rates (e.g. from $v=0.2..4$ m/s for CH₄/air) and air/fuel relative ratios (e.g. from $\lambda=1..2$ for CH₄/air). Depending on the application, a third stage may be directly added to the burner, with a compact heat exchanger.

The wide power modulation capability of porous burners make them ideal for applications such as home water heaters, where the power needed to heat sanitary water cannot be less than say 15 kW and is increasing, whereas the power for space heating is decreasing from typically 20 kW to 5 kW for better-insulated apartments. Besides, being more compact, porous burners could be installed in wall niches instead of protruding significantly. This compactness is also an advantage for industrial heaters and driers, that must be 1 m to 3 m long if conventional (to protect from the flame), but can be shorten to less than 0.5 m using a porous burner.

FLUIDISED BED COMBUSTION

Fluidised bed combustion is conceptually similar to porous burner combustion, but, instead of a rigid solid matrix, a high-temperature combustion takes place within a particulate system (the fuel particles themselves, or sand or other granular refractory), held over a porous surface. When an upward air-stream (or a premixed fuel/air stream) is established, for small upward speeds the particulates act just as a filter, but when the drag on the particles overcome its weight, a fluidised regime is establish (at the fluidising speed), with more or less ‘bubbling’ or ‘boiling’ when speed is increased until at a certain value is reached (the terminal velocity) beyond which the particles are ejected from the bed and carried away with the stream.

The main advantage of this modern type of combustors is that additives can be easily added and the porous material easily refurbished. The disadvantages are the difficult start-up, difficult ignition (it is ignited above the bed), noise, and erosion of the heat-exchanger walls (that is partially or totally submerged to limit the maximum temperature within the bed). Steady burning is achieved at 1100 K to 1300 K (uniform red-hot bed), but below 1100 K the burning is noisy with violent small bursts, and above 1300 K the particulate may start fusing and clogging. Fluidised bed combustion is currently used in some coal-fired power plants, where coal-desulfuration is achieved during combustion by adding lime to the bed. It is also been used to burn high-moisture fuels like agriculture and industrial residues and sludge.

OPEN FIRES

Most practical combustion systems are enclosed inside easily-identifiable walls (combustion chambers, empty or filled with porous media). By 'open fires' we here just mean unenclosed combustion setups, from the traditional fireplace to the wild uncontrolled forest fire, passing by the humble candle flame. Because the information here compiled is basically historical, it can be found under “Torches, oil lamps and candles”, in [Fuels](#).

Smouldering is not intentionally used in engineering, but it is very important in uncontrolled fires. Porous materials, either solid like wood or particulate like dust, may sustain a low-temperature combustion inside with air penetrating by diffusion. A smoulder temperature may be identified to describe the flammability behaviour of a flat dust layer on a hot surface (e.g. the lowest temperature of a heated surface capable of igniting a 5 mm thick dust)

COMBUSTION HISTORY (WHAT WAS KNOWN)

Although the history of combustion is related to the history of fuels, we treated them here separately because under 'fuels' we focused on empirical findings and under 'combustion' we centre the attention on theories.

FUEL HISTORY

This theme can be found in [Fuels](#). Briefly, Fuel history has the subheadings there: Biological fuels before the XX c., Mineral fuels (coal, crude oil and natural gas), and Biological fuels in the XXI c.

HISTORY OF COMBUSTION THEORIES

Fire has always been a cause of panic, but also of immense power. It had a magical appeal: Prometheus stole it from the gods, according to Greek mythology. Around 500 b.C., Heraclitus of Ephesus held that fire is the primordial substance of the universe and that all things are in perpetual change (like a vital flame). Around 450 b.C., Empedocles of Sicily set the theory of the four universal elements: fire, air, water, and earth, further developed and spread by Aristotle around 350 b.C. (he added aether as the quintessence, in his *Metaphysics*).

Coming down to our physics, it was appreciated from the beginning that combustion required a fuel (e.g. wood, but not stone) and an igniter (by rubbing woods, sparking stones or compressing air, but not just hitting the wood). However, it was only learnt in the 17th c. that air was also needed; around 1663, Boyle realised that, under vacuum, sulfur could not be ignited by concentrated light, as usually achieved, but it was Lavoisier in 1777 the first to realise that oxygen was the key, both to combustion and to animal respiration. Much earlier than the need of air for combustion was realised, it was common practice to preserve fire overnight by putting a fire cover (curfew) over it, to avoid air convection and heat loss.

The concept of energy (chemical, thermal, electrical), as an extension of the primitive mechanical idea of combination of 'head' (potential energy) and 'vis viva' (kinetic energy), was only generally accepted after mid 19th century. Before that, imaginary fluids were thought to explain the facts. Around 1660, J.J. Becher and G.E.Stahl introduced the theory of phlogiston as a fluid that flowed away in combustion processes. Lavoisier, in his paper "Réflexions sur le phlogistique" of 1783, rejected the phlogiston theory, but set forth the caloric theory, a fluid that flowed away with heat (some authors even advocated for another fluid for cooling processes, the frigoric). Although already in 1798, Count Rumford rejected the caloric theory in his essay 'An experimental enquiry concerning the source of the heat which is excited by friction', it was not until the 1840s that it was finally discarded and replaced by the principle of energy conservation, by Mayer and Joule.

A good appreciation of the level acquired in combustion theory can be grasped from the titles of Michael Faraday's famous series of Christmas Lectures for Children, delivered in the mid 19th c. (starting in 1826) at the Royal Institution. The most important (actually six of them) was published as "The Chemical History of a Candle" in 1860:

1. Construction of a candle. The flame.
2. Necessity of air for combustion.
3. Products of combustion; water from combustion.
4. The components of water are oxygen and hydrogen.
5. Components of air: oxygen and nitrogen. Product from a candle: carbon dioxide.
6. Human respiration and its analogy to a candle.

A summary of the chronological development of combustion theory is presented in Table 2.

Table 2. Chronology of combustion theories.

The need of air	Robert Boyle-1663 found that combustion requires air, besides the fuel.
Phlogiston	<p>Proposed by the German physician and chemist Georg Ernst Stahl-1697 and discarded by Antoine Lavoisier-1783-Réflexions sur le phlogistique, (lat. <i>phlegma</i>=fire spirit): a substance (with mass) stored in fuels and released in chemical reactions (the flammability component), aside of the caloric substance (the heating component). Fuels released phlogiston quickly, whereas metals did it slowly (rust). Afterwards, Joseph Priestley-1796 tried to come back to phlogiston.</p> <p>Phlogiston principles:</p> <ul style="list-style-type: none"> • Phlogiston is a material fluid present in fuels (wood, coal, metals and living beings), that escapes from them when bodies are heated to burn. • Air is a phlogiston absorber, needed to let it escape from fuels. If air is trapped inside a bell, fuels cannot yield all their phlogiston. Plants slowly take phlogiston from the air on sunshine, and may suddenly release it if burned. • Phlogiston is conserved; e.g. animals exhalate phlogiston by the mouth, is stored in the air and plants, and returns to animals when they eat plants, or to air if plants are burnt. The phlogiston released by metals when rusting may be fed-back from phlogiston-containing substances (metals are obtained from their ores by calcination with wood or coal). Water dissolves phlogiston, but does not destroy it. • Phlogiston can be weighted by difference before and after burning the fuel. But metals release so little phlogiston that it floats in air, making the metal heavier when rusted. <p>Question. What was phlogiston: H₂ (released by metals when pouring an acid over) CO₂ (exhaled by animals), or O₂? Answer: the closest idea is to -O₂, i.e. oxygen affinity.</p>
Caloric	Proposed by Lavoisier-1777 and discarded by Mayer-1842, a substance (with mass) released in thermal processes. Similarly, electricity was a substance (with mass) released in electrical processes.
Mass conservation	Proposed by Lavoisier-1777: the overall mass is preserved in any confined chemical reaction. He also established the taxonomy of chemical compounds, and identified oxygen-in-the-air as the main oxidiser, and carbon and hydrogen as the main fuel-constituents.
Fixed	Proposed by Proust-1799: chemical reactions take a fixed amount of substances

proportions	relative to another, and the excess appears un-reacted (quite different to a mixture).
Multiple proportions	Proposed by Dalton-1803: different chemical reactions between same reactives take a fixed amounts of substances relative to another, the ratio between which are small whole numbers. Berzelius-1826 accurately measured the relative masses in chemical reactions and established chemical-formula notation (the first letter of the Latin name with the relative factor as a superscript, later changed to subscript, e.g. H ₂ O).
Flame quenching Emissions	Sir Humphry Davy published in 1800 his personal trials on the physiological effects of some gases of importance to combustion (laughing gas, NO, and water gas, i.e. CO+H ₂ , which nearly poisoned him). Around 1815 he discovered that flames cannot go through wire meshes and developed the miner's safety lamp.
Premixed flame Flame spectra	Robert Bunsen, Prof. At Heidelberg, developed his premixed burner in 1855, measuring flame temperatures and flame speeds. Bunsen-1860 repeated Newton's experiment of light dispersion by a prism, but with the light of flame, and discovered that it was not a continuum but separated bands, particularly with premixed flames, and the bands changed with addition of different substances to the flame (the spectrum was characteristic of the substance). Bohr-1913 proposed the orbital theory of electrons in the atom, the quantum numbers, and explained the emission spectra of simple atoms in absence of magnetic fields (quantum mechanics explains everything up to now).
Thermal model	Mallard and Le Châtelier, Profs. at École de Mines de Paris, studied flame propagation in 1868 and proposed the first flame structure theory in 1883. Chapman and Jouguet in 1900 distinguished deflagrations from detonations and computed detonation speeds. Thermal Ignition: Semenov's theory of 1928 (uniform temperature), Frank-Kamenetskii's theory of 1945 (with thermal gradients). Thermal explosions. Zeldovich theory of 1943. He also proposed in 1943 his thermal model for the formation mechanism of NO.
Diffusion model	Burke and Shumann in 1928 made the first theoretical computation of non-premixed flame height and shape.
Thermal-diffusive model	Zeldovich in the 1940s and Sivashinsky in the 1970s analysed thermal-diffusive instabilities in two-dimensional flames.
Thermo-fluid-chemistry theory	Theodore von Kármán, the founder of the U.S. Institute of Aeronautical Sciences (1933), of the Jet Propulsion Laboratory (1944), and a co-founder of the Combustion Institute, organised and led (under NATO and UN auspices) an international team, around 1950, to compile and spread multidisciplinary knowledge on combustion science, producing his famous Aerothermochemistry notes and lectures (T. von Kármán and G. Millán, Proc. Combust. Instit. 4, 173 (1953)).
Finite rate chemistry	Asymptotic methods for different chemical and flow time scales: activation energy and reaction-rate ratio asymptotics. Steady-state and partial-equilibrium approximations.
CFD codes	Simulation of multidimensional reacting fluid flow, including turbulence, unsteadiness, multiphase flow, acoustic-coupled instabilities, etc.

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