POLLUTION CONTROL THROUGH EFFICIENT COMBUSTION TECHNOLOGY

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Contents

Summary

Pollution from combustion processes is mainly related to incomplete combustion, losses of fuel, or the presence of hetero-elements in the fuel. A survey is given of these factors and waste incineration is briefly introduced in this chapter.

This chapter also reviews combustion fundamentals, chemistry of combustion, transport properties and combustion research (see *Combustion Fundamentals*, *Fundamentals of Transport Phenomena in Combustion*, and *Combustion Research and Computer Fluid Dynamics*). Thermal and catalytic combustion, economic, practical, and safety aspects are described in detail in *Thermal and Catalytic Combustion*. *Management of Combustible Waste* reviews waste management, and *Waste Incineration Technology* is devoted to the technology of the incineration.

1. Combustion Concepts

1.1 History of Combustion Science

Combustion is an essential process in numerous activities, and its control paved the way towards technical and industrial development. Neolithic humans mastered ignition, using friction-producing implements or flint struck against pyrites. Since fire was first discovered, humans speculated about its nature and properties, in terms of either philosophical doctrines or experimental techniques. Aristotle considered fire, water, earth, and air to be the four essential elements of all things. The phlogiston theory even conceived fire as a material substance, having weight. Lavoisier discovered that the combustion products of sulfur or phosphorus outweigh the initial substances and postulated that their increased weight was due to the combination with oxygen from air. This theory was based on the **law of the conservation of matter**. Lavoisier clarified the concept of a **chemical element**, Dalton compiled the first table of **atomic weights**, and other scientists discovered new gases. These findings supported experimental study of chemistry, based on accurate measurement. Thompson's experiments revealed evidence for the concept of **heat** as a movement of particles, eventually leading to the **kinetic theory of gases**, based on the premise that heat results from motion of molecules and atoms. Later, **thermodynamics**, especially **thermochemistry,** allowed elucidating the energy aspects of combustion. Davy first measured flame temperatures, investigated the effect of dilution with various gases on flames and discovered **catalytic combustion** on surfaces, accompanied by the release of heat but without flames.

Investigating the combustion of gas mixtures and their burning velocities, free radicals and ions generated by the thermal dissociation of gas molecules (see *Combustion Fundamentals*) was essential for developing theories concerning combustion mechanisms. The Bunsen burner led to the study of flame structure. Explosion hazards in coal mines had drawn attention to **flame propagation**, when Davy invented his safety lamp. In 1881 detonation was discovered and led to the theory that a gas under certain conditions can be compressed and then ignited by the resulting rise in temperature. **Chemical kinetics** after the 1930s became an indispensable part of **flame propagation** theory and modern computing tools not only can model the chemical processes in a flame, but also combine these with fluid dynamics and heat and mass transfer.

1.2 Combustion and Oxidation

Combustion is a generic group of fast chemical reactions, involving combustible materials or **fuels** as some of the reactants, oxygen from air as the other. It is a source of heat and usually of light, in the form of **flames**. Fuels are gaseous, liquid, or solid, but all flammable materials sustain combustion, when sufficiently dry and preheated to some suitable ignition temperature. Even most metals burn, when finely divided or heated to sufficiently high temperatures. Metal bearing catalysts are often **pyrophoric**, i.e. ignite at the contact with air. Magnesium metal was used for flash lighting in early photography; aluminum and iron serve as metallurgical reducing agents and finely divided Raney nickel catalyst, used for hydrogenation, burns in air at room temperature. Massive iron and steel, however, have to be locally preheated by an oxygen/acetylene torch; at a suitable temperature combustion continues with supply of oxygen only.

Combustion is also a form of **oxidation**, i.e. in an etymological sense, a combination with oxygen. In chemistry the concept of oxidation has been enlarged, however, to any reaction accompanied by a loss of electrons. The frontier between combustion and oxidation is somewhat loosely defined, and related to two characteristics of combustion - being fast and liberating lots of heat.

To the engineer **combustion** is a chemical union of fuel and **oxygen**, controlled to produce useful heat. Air is a free and standard source of oxygen. For reaching high combustion temperatures pure oxygen or oxygen-enriched air are used. The cost of oxygen is partly compensated by the much lower volume of gas to be moved and eventually purified. Combustion is also sustained by chlorine, fluorine, and other strong oxidants, such as nitric acid, nitrates (black powder), peroxides or perchloric acid. In such cases combustion could better be termed a fast, sometimes explosive oxidation. Numerous substances so readily burn in oxygen that this oxidant becomes a hazardous substance in its own right, e.g. in steel industry, petrochemical industry, and where used for medical purposes.

If there is more air than the theoretical amount required combustion is **fuel-lean.** Excess air is normally required to obtain (reasonably) complete combustion.

If fuel is supplied in excess, combustion proceeds under reducing or **fuel-rich** condition. A fuel-rich flame forcibly leads to incomplete combustion and – unless sufficient care is taken – unburned fuel, carbon monoxide, polycyclic arenes (Polycyclic Aromatic Hydrocarbons, PAHs) and other Products of Incomplete Combustion (PICs) are emitted, albeit in amounts that are rather unpredictable.

1.3 Ignition

A flammable mixture of combustible gases and air may be stored for centuries without notable changes in composition. Yet, a spark, a hot wire or surface, a match, a pilot flame, friction, or even light, ignite such a flammable mixture and burn it in only fractions of a second. The minimum energy required for ignition is very small and shows a sharp minimum close to the stoichiometric composition. Ignition is a logical starting point in studying combustion and its various chemical and physical aspects.

Ignition starts from local heating of a fuel/air-parcel that reacts, liberating heat in the process. Such local heat generation tends to communicate to adjacent parcels where ignition may take place. Gaseous fuels are easily ignited, when their concentration is situated between a **L**ower **E**xplosion **L**imit **(LEL)** and an **U**pper **E**xplosion **L**imit **(UEL)**, respectively corresponding to the lowest gas concentration, still sustaining combustion, and with the highest, above which combustion air becomes inadequate to sustain the process. Liquid fuels are classified according to their **flash point** and **flame point**. At these temperatures a liquid generates enough volatile vapors, respectively to briefly enhance an externally generated spark, or have its vapors ignited. If the flame point is well above ambient (kerosene, oil) ignition is no longer an easy process. However, if fuels are atomized, they behave as if their vapor pressure is much more elevated. Likewise, as solid combustibles are heated, they thermally decompose, generating flammable gases and vapors, and active combustion only starts when evolving fuel gases and vapors are available in sufficient amounts and ignited. Coke and anthracite are lean in volatiles and hence difficult to ignite.

Ignition spreads from its source to adjacent gas or vapor, further propagating into the surroundings as long as some necessary conditions for combustion simultaneously are being met: the state of the system of fuel and oxidizer is characterized by a specific combination of temperature, pressure, and concentration (the three principal parameters of state, which are interrelated) and the rate of heat generation is at least equal to that of heat dissipation to the surroundings. Combustion theoretically terminates when thermodynamic equilibrium is achieved, i.e. when conversion is essentially complete. In practice, however, a fire extinguishes well before reaching equilibrium, because heat generation becomes insufficient to maintain the process when most materials are already burnt, or because of excessive cooling of the flame, important instabilities in the flame, or the impact of free radical consuming walls or extinguishing powders, water, or inert gases.

Although it seems such a natural and spontaneous process, combustion is sustained and propagated by extremely complicated systems of branched-chain **free radical reactions**, even in apparently simple cases, e.g. in hydrogen or carbon monoxide combustion, usually presented with their global molecular interactions:

$$2\,H_2 \quad + \quad O_2 \quad \Rightarrow \quad 2\,H_2O \qquad (1)$$

$$2\,CO \quad + \quad O_2 \quad \Rightarrow \quad CO_2 \qquad (2)$$

In fact, the global reaction (1), for instance, requires nearly 40 elementary reactions for describing the chemical mechanism. In other words, simple systems are incorporated into more complex ones, accounting for combined pyrolytic and oxidative breakdown of hydrocarbon molecules (see *Combustion Fundamentals*).

In addition to complex chemical processes **physical processes** that transfer mass and energy are also most important in combustion and closely coupled with chemical ones.

In diffusion flames for example, involving a non-premixed mixture of fuel and air, the **diffusion** of reactants and combustion products is rate-determining and depends on concentrations, pressure and temperatures, and diffusion coefficients. **Convection** is largely responsible for the **transport of mass** and (together with radiant heat) also of **energy**, and comprises buoyant and external forces, as well as **turbulent and eddy motions**. Rates in heat and mass transfer (see *Fundamentals of Transport Phenomena in Combustion*) are derived under the form of empirical correlations featuring dimensionless groups, such as:

- The Reynolds Number, characterizing flow conditions,
- The Prandtl and Schmidt Numbers, featuring physical properties combined to a dimensionless entity, respectively relevant in heat and mass transfer;
- The Nusselt and Sherwood Numbers, describing important rate ratios in heat and mass transfer, respectively.

Combustion may emit **light**, mostly in the **infrared portion** of the spectrum, and associated with the major combustion products carbon dioxide and water vapor. Light also arises from the presence of particles in **electronically excited states** and from normally unstable species such as **ions, radicals**, and **electrons**. Radiation is important in heat transfer and becomes rate determining in heat transfer at flame temperature.

1.4 Flames and Flame Propagation

Flames are composed of a rapidly reacting mixture of air and flammable gas or vapor, giving off heat and light. Flames often appear in active combustion and are characterized by geometry, form and position of the flame axis, stability, buoyancy, and radiant heat loss.

For safety reasons (no flash back possible) diffusion flames are generally preferred over premixed flames. Gas burners typically feature a central duct, with a gas exit velocity of 50 - 200 m s^{-1} for natural gas. Combustion air is supplied at a much lower velocity through an annular aperture surrounding the first. The major flame characteristics are length, angle, stability, and radiant properties. They mainly depend on the methods used for mixing gas with air. Mixing is the determining parameter which means that, practically speaking:

$$\textit{Mixing rate} = \textit{Combustion rate} \qquad (3)$$

For industrial burners, flow conditions are turbulent and determine mixing rates and patterns. A single gas flame can be regarded as a free jet, emerging into a furnace with much larger cross-section. The flame geometry depends on the size and form of the orifice, the outlet velocity, the amount and swirl of combustion air. Flame position and shape are adapted by varying the position or angle of injection, combining several burners in-line, the radial or tangential positioning, e.g. in the corners of a corner fired furnaces. There is interaction between a burning jet and its surroundings, with entrainment of adjacent air and possibly formation of re-circulating currents.

The highest combustion rate is attained at about one third of the flame length. This length can be reduced by partial pre-mixing of fuel and air, increasing the swirl, feeding fuel and air under an angle, or preheating the combustion air. The flame is lengthened by increasing the momentum of the fuel injected, adding re-circulated flue gas, and diluting the stream to be fired.

Sometimes combustion arises undesirably and/or spontaneously. This is the case with accidental fires, arson, the breeding of hay or other combustible solids, and with gas, vapor, oil mist, or coal dust explosions (see *Thermal and Catalytic Combustion*). Uncontrolled combustion and **explosion** occur as a consequence of self-accelerating effects, triggered by liberation of heat in excess of the amount that can be dissipated to the surroundings.

Fuel	Rate of Flame Propagation	
	In Air, cm s^{-1}	In Oxygen, m s^{-1}
Carbon monoxide	$17.4^{a} – 19.5^{b}$	330
Methane	$42^{a} – 43^{b}$	360
Propane	$46^{a} – 47^{b}$	100
City gas	$86^{a} – 103.5^{b}$	-
Acetylene	$155^{a} – 165^{b}$	1340
Hydrogen	$237^{a} – 364^{b}$	890

[Source: Günther R. (1974) *Verbrennung und Feuerungen*. Berlin – Heidelberg - New York: Springer-Verlag]

[a] refers to stoichiometric mixtures

[b] refers to the maximum laminar rate velocity, to be obtained for slightly rich mixtures

Table 1: Rates of Flame Propagation: the Laminar Flame Velocity in Air and Oxygen.

Flame propagation is explained by two theories, based respectively on **heat conduction** and on **diffusion of reactive species** as the principal means of igniting a flammable mixture. Combustion propagates from the flame front, the area in which active combustion occurs, to the still unburned mixture of fuel and air. In the first theory heat from combustion flows to the inner core, whereas the second sees mainly molecules produced in the reactive flame front diffuse into the inner cone and ignite the mixture. In reality, both always occur in combination.

The **flame velocity (laminar burning velocity)** is the characteristic rate at which a flame progresses into the unburned premixed mixture of fuel and oxidizer. Basically, it depends on fuel type, air equivalence ratio, pressure, and initial temperature. Zeldovich derived a theoretical formula for flame velocity as:

$$v_{\mathrm{flame}} = \{[k_{\mathrm{o}}\, Q_{\mathrm{molar}}\, e^{-E/RT}\, RT/E]/(T_{\mathrm{i}} - T_{\mathrm{o}})^2\}^{1/2} \qquad (4)$$

with

v_{flame} = laminar flame velocity, m s^{-1}

k_{o} = heat conductivity of the fuel/air-mix, W m^{-1} K^{-1}

Q_{molar}= molar reaction heat, J mol^{-1}

T = adiabatic flame temperature, K

T_{o} = temperature of the fuel/air-mix, K

T_{i} = ignition temperature, K.

Most hydrocarbons burn with laminar flame velocity of the order of 0.5 m s^{-1}. Oxygen enrichment, reactive species and high flame temperatures increase this flame velocity. The adiabatic flame temperature must attain ca. 1700 K to ignite the surroundings. The influence of pressure is rather complex.

Flame fronts will not adhere to walls. Flame propagation is halted in the presence of cold surfaces, absorbing heat and radicals. Within a limit distance from the wall flame velocity becomes nil.

It takes a distance L to attain full flame velocity, with L proportional to k_o and inversely proportional to ρ_o, c_p and v_{flame}. Turbulence enhances heat and mass transfer, increasing v_{flame}. Conversely, combustion creates turbulence.

Flames may be extinguished by excessive cooling as well as various other causes, such as strain, due to extreme turbulence.

1.5 Burners

A burner has three functions:

- Mixing fuel and air in appropriate proportions,
- Providing a suitably shaped section for flow of fuel and air,
- Act as a heat sink to restrict erratic movements of flame. The stabilizing effect is provided by a rim, removing heat and free radicals and reducing the burning velocity.

Gas burners are deceptively simple. **Premixed gas burners** consist of a tube, with their orifice fitted with a porous gas distributor or screen plate, protecting against flame-flashback into the tube.

Diffusion burners introduce the gas at a linear velocity of 50-200 m s^{-1}, much larger than the flame velocity through a central jet. Combustion air leaves an annular duct surrounding the jet at much lower speed, below 10 m s^{-1}. The flame characteristics are defined by mixing mechanisms.

Figure 1 shows a cross-section of the flame, and the corresponding concentration profiles of fuel and oxygen. Gas G flows from the burner tube, emerging as a free jet (Figure 1, left), and mixes with the air A entrained by this jet (mixing zone G + A). Once ignited, three distinct zones are formed in and around the flame: outer Air A, inner Gas + Combustion Products (zone G + P) and the intermediate Air A + Combustion Products (zone A + P).

Stable combustion is only possible by adapting flow conditions, mixing of air and gas, and ensuring the ignition of flammable mixtures once formed. Figure 1, right shows the concentration of oxygen, carbon dioxide formed, and gas, according to a cross-section noted A – A through the flame front.

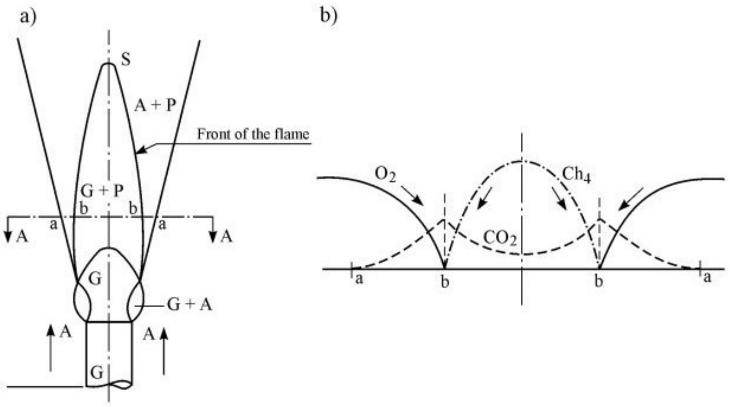

Figure 1: Cross-section of (a) a non-premixed flame, (b) corresponding concentration profiles of fuel and oxygen.

The flame features are readily explained by the spontaneous mixing of gas and surrounding air, without artifices to stabilize the flame, or provisions for inducing swirl.

Optimal operation of **oil burners** is of paramount importance for the environment. Unfortunately, in industrial practice too many burners are ill tuned and often operate out of their optimal range, possibly with

- lavish excess of air, lowering combustion temperatures, rates of radiant and convective heat transfer, as well as boiler efficiency (due to higher stack losses),
- inadequate atomization of oil.

Tiny droplets well below 30 micrometers in diameter burn almost as a vapor cloud, ensuring good combustion efficiency as well as large radiant heat transfer rates. Large oil droplets, resulting from poor atomization (see *Wet Scrubbers*) lead to black sooting flames. Normal residence times will not suffice for ensuring complete combustion of the carbon in them, with subsequent soot emission. The following procedure may help the control of pollution:

- Checking conditions of fuel atomization (e.g. cleaning the burner, verifying the flow of auxiliary atomizing air or steam, and the viscosity or the preheat temperature of the oil),
- Promoting post-combustion of soot particles by providing prolonged residence times and adequate turbulence at sufficiently high temperature, or recycling flue gases.

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Biographical Sketch

Alfons Buekens was born in Aalst, Belgium; he obtained his M.Sc. (1964) and his Ph.D (1967) at Ghent University (RUG) and received the K.V.I.V.-Award (1965), the Robert De Keyser Award (Belgian Shell Co., 1968), the Körber Foundation Award (1988) and the Coca Cola Foundation Award (1989). Dr. Buekens was full professor at the Vrije Universiteit Brussel (VUB), since 2002 emeritus. He lectured in Ankara, Cochabamba, Delft, Essen, Sofia, Surabaya, and was in 2002 and 2003 Invited Professor at the Tohoku University of Sendai.

Since 1976 he acted as an Environmental Consultant for the European Union, for UNIDO and WHO and as an Advisor to Forschungszentrum Karlsruhe, T.N.O. and VITO. For 25 years, he advised the major industrial Belgian Bank and conducted more than 600 audits of enterprise.

Main activities are in thermal and catalytic processes, waste management, and flue gas cleaning, with emphasis on heavy metals, dioxins, and other semi-volatiles. He coordinated diverse national and international research projects (Acronyms Cycleplast, Upcycle, and Minidip). Dr. Buekens is author of one book, edited several books and a Technical Encyclopedia and authored more than 90 scientific publications in refereed journals and more than 150 presentations at international congresses. He is a member of Editorial Boards for different journals and book series.

He played a role in the foundation of the Flemish Waste Management Authority O.V.A.M., of a hazardous waste enterprise INDAVER, and the Environmental Protection Agency B.I.M./I.B.G.E. He was principal ministerial advisor in Brussels for matters regarding Environment, Housing, and Classified Enterprise (1989). Since 1970 he has been a Member of the Board of the Belgian Consumer Association and of Conseur, grouping more than a million members in Belgium, Italy, Portugal, and Spain.

He is licensed expert for conducting Environmental Impact Assessments (Air, Water, Soil) and Safety Studies regarding large accidents (Seveso Directive).