COMBUSTION FUNDAMENTALS

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Summary

This chapter is devoted to some fundamental aspects of combustion. Important concepts, based on air equivalency, heat of reaction, and thermal decomposition are explained and the physical and chemical aspects of combustion are analyzed.

Finally, attention is paid to various aspects of premixed and diffusion flames and to similarities as well as distinction between firing gases, liquids, and solid fuels.

1. Basics

1.1. Air Equivalence Ratio

Combustion can proceed under either fuel-rich or fuel-lean conditions. If fuel is supplied in excess, combustion proceeds under reducing or **fuel-rich** condition; if there is more air than the amount theoretically required it is oxidizing or **fuel-lean**. It is **stoichiometric** (or neutral) if both fuel and air are metered and mixed in such a way that they consume each other completely. Almost always, however, there is some deliberate excess of one of the two reactants, generally air, which is inexpensive and anyway required to complete combustion. Fuel-rich flames forcibly lead to incomplete combustion so that unburned fuel, carbon monoxide (CO), Polycyclic Aromatic Hydrocarbons (PAHs) and other Products of Incomplete Combustion (PICs) are emitted, albeit in relative amounts that are rather unpredictable, varying with the quality of mixing and post-combustion.

In most cases the oxidizer is air, composed of about 21 % by volume of oxygen, 78 % by volume of nitrogen, and 1 vol. % of argon, and other noble gases. Hence, the sum of the inert gases equals 79/21 or 3.76 times the volumetric amount of oxygen. Excess air is generally characterized by the **air equivalence ratio**, also *air number*, or *air factor*, often denoted k (or λ, or α). The inverse **fuel equivalence ratio** is generally noted as $\Phi = 1/k = 1/\lambda$. A k-value of 1.15 means an excess of air over stoichiometric conditions of 15 %. Extra air cools the flame and dilutes the flue gas.

A fuel-lean flame has oxygen in excess of theoretical requirements and combustion is likely to be more complete, unless so much excess air is supplied that the flame gets too much cooled and the residence time in the furnace is shortened by the larger flow of gases. At that moment, adding more air raises both non-combusted fuel and Products of Incomplete Combustion (PICs) levels. A distinction between both is difficult to handle in practice, because some compounds may both be present in the original fuel (benzene, PAHs) and be formed as PICs. Analyzing off-gas does not allow distinguishing between both.

Ideally, combustion proceeds with appropriate levels of air excess; the latter is selected lower in case combustion proceeds easier. Hence this excess of air rises in a sequence gas < liquid < solid fuel firing. However, it also depends on the way fuel is supplied and treated: firing pulverized coal is entirely different from firing lump coal, a pool burner different from one atomizing the liquid fuel to the finest droplets. Fuel aerosols are almost as reactive as gaseous combustibles; large fuel parcels burn at high rate and

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create oxygen deficiencies. Secondary combustion air is often injected at high speed, ensuring an adequate mixing of fuel-rich and fuel-lean strands of combustion products. Other possible tasks for combustion air are grate, burner, and wall cooling, and avoiding adherence of tacky deposits.

Theoretical air requirements and the resulting flue gas composition are derived from stoichiometric relations, such as:

$$H_2 + 0.5\,[O_2 + 3.76\,N_2] \rightarrow 0.5\,H_2O + 0.5\,x\,3.76\,N_2 \quad (1)$$

$$CH_4 + 2\,[O_2 + 3.76\,N_2] \rightarrow CO_2 + 2\,H_2O + 2\,x\,3.76\,N_2 \quad (2)$$

$$C_3H_8 + 5\,[O_2 + 3.76\,N_2] \rightarrow 3\,CO_2 + 4\,H_2O + 5\,x\,3.76\,N_2 \quad (3)$$

$$C_xH_y + (x + y/4)\,[O_2 + 3.76\,N_2] \rightarrow x\,CO_2 + 0.5\,y\,H_2O + (x + y/4)3.76\,N_2 \quad (4)$$

As the fuel molecules become larger, more combustion air is needed, diluting the fuel/air-mix. A stoichiometric mixture hydrogen/air contains 29.6 volume percent of fuel. This figure reduces to 9.50 for methane, 4.03 for propane and some 1.6-1.9 for gasoline.

1.2. Energy Balances

The Law of Conservation of Energy states that there is always equality in a system between

[*Sum of all Inputs*] = [*Sum of all Outputs*] + [*Accumulation*] (5)

Distinction can be made between:

- **chemical energy** stored in the fuel molecules,
- **sensible heat** available in these and the combustion products,
- **latent heat**, relating to a change of state of the materials involved, and
- **heat losses** of the combustion plant to the outer world. The latter typically range from few to typically 5–20 %, depending upon the quality of thermal insulation.

Chemical energy, **enthalpy** or **internal energy** H is liberated in the combustion process.

Sensible Heat is accumulated in a material when it is heated above standard conditions. Integrating the molar heat capacity C (J mol^{-1} K^{-1}) or the mass heat capacity c (J g^{-1} K^{-1}) over the relevant temperature interval, starting from an arbitrary state of reference (usually 25° C for thermodynamic data or 0° C for physical data) to the actual temperature considered, yields this sensible heat.

Latent Heat is associated with phase changes, such as evaporation, sublimation, or melting and expressed on either a molar or a mass basis. The most important contribution stems from water vapor, which has sizeable heat of evaporation. The latter is rarely recovered, since operating below the dew point requires corrosion-resistant materials, such as glass or plastics.

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1.3. Heat of Combustion

The **Heat of Combustion** (or Reaction) is tabulated for most fuels and their reaction products and available as graphs, or formulas. It is readily derived from a few thermodynamic properties of state.

Methane:	56 MJ kg^{-1}
Propane:	50 MJ kg^{-1}
Gasoline (approx.)	48 MJ kg^{-1}
Diesel oil (approx.)	45 MJ kg^{-1}
Anthracite (approx.)	33 MJ kg^{-1}
Bituminous coal (approx.)	30 MJ kg^{-1}
Methanol:	22 MJ kg^{-1}
Wood (approx.)	15 MJ kg^{-1}

The **Heat of Formation** H_f is the heat liberated, if a compound were formed from its elements, all considered at standard conditions. By convention, the heat of formation of elements (carbon, hydrogen, oxygen, etc.) is zero in their standard state, and a reaction is exothermic (liberating heat) when it is associated with a *negative* enthalpy effect, e.g.

$$C + O_2 \rightarrow 44\,g\ \text{of}\ CO_2 \quad ; \quad \Delta H_{298} = -94.03\,\text{kcal} \qquad (6)$$

$$C + \tfrac{1}{2} O_2 \rightarrow 28\,g\ \text{of}\ CO_2 \quad ; \quad \Delta H_{298} = -26.4\,\text{kcal} \qquad (7)$$

Data for the heats of formation of the main participants in combustion reactions can be found in most specialized handbooks.

The heat of combustion is derived by subtracting the heat of formation of reactants from that of products, taking into account their relative molar amounts. Implicitly, this concept is based on the Law of Hess, stating that the thermal effect of a process only depends on nature and condition of both starting and final products. For the sake of example, burning ethyl alcohol proceeds by the following reaction:

$$C_2H_5OH\,(g) + 3\,O_2\,(g) \rightarrow 2\,CO_2\,(g) + 3\,H_2O\,(l) \qquad (8)$$

The computation is based on the following heats of formation:

$$\text{INPUT} \quad 3\,C + 3\,H_2 + \tfrac{1}{2} O_2 \rightarrow C_2H_5OH\,(g) \qquad (9)$$

$$\text{OUTPUT} \quad \begin{array}{l} 2\,C + 2\,O_2 \rightarrow 2\,CO_2\,(g) \\ 3\,H_2 + \tfrac{3}{2} O_2 \rightarrow 3\,H_2O\,(l) \end{array} \qquad (10)$$

In this example ethanol vapors generate more heat of combustion than liquid ethanol: the latter absorbs latent heat of evaporation before turning to vapor.

1.4. Adiabatic Flame Temperature

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The adiabatic flame temperature is derived by equalizing the heat of combustion and the enthalpy of the resulting reaction products as a function of temperature. These temperatures are quite high, but still restrained by some thermal decomposition of the 'stable' reaction products:

- Hydrogen/oxygen: 2 810° C
- Carbon oxide/oxygen: 3 000° C
- Acetylene/air: 2 250° C
- Hydrogen/air: 2 107° C
- Methane/air: 1 949° C

The equilibrium composition of H_2O, CO_2, CO, O_2, H_2, OH, H, O, NO, N_2 at flame temperature can be found in the specialized literature. About one quarter of the gas consists of hydrogen and oxygen atoms and hydroxyl ions and the burnt gas conversion is only 57 percent. The equilibrium CO/air mix contains 35 percent of unchanged carbon monoxide.

1.5. Thermal Decomposition of Organic Compounds

Organic compounds in fuels, waste, or materials in an accidental fire thermally decompose, by complicated chemical mechanisms, influenced by numerous physical parameters. Relevant reactions are subdivided into:

- **Primary processes**, involving the parent molecule, and
- **Secondary reactions**, i.e. further conversion of primary products, or reactions between such products and parent molecules. Secondary reactions are monitored by observing the products in a reacting system as a function of time, while other factors (e.g. temperature) remain constant.

These main factors of influence are:

- **Temperature**

Higher temperatures enhance the rate of decomposition. Temperature also influences upon thermal stability of parent and product molecules and the rates of further reactions.

- **Time of reaction**

At very short reaction times only primary products are found, but as time proceeds secondary products take over, sometimes obscuring identity, and amounts of primary products. In cellulose pyrolysis its monomer levoglucosan is best detectable at short reaction times and low pressures, because it disappears in secondary polymerization reactions.

- **Pressure**

Pressure mainly influences upon the relative amounts of volatiles and non-volatile products. Higher pressure yields heavier products of decomposition.

- **Composition** of the gas atmosphere

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Traces of reactive gases, such as oxygen and hydrogen, may initiate radical reactions, whereas inert gases have similar effects as a decrease of the pressure, even though they may help in stabilizing unstable molecules. At temperatures above 800° C also water vapor and carbon dioxide become capable of oxidizing carbon and depressing soot formation.

- **Rate of heating**

The rate of heating determines yield and selectivity of the primary and secondary products, but its influence varies markedly with the system being considered. Laboratory equipment, such as pyrolysis gas chromatography, allows heating at rates in excess of 1000° C per second, simulating flash pyrolysis. Conversely, TGA (Thermogravimetric Analysis), DSC (Differential Scanning Calorimetry) and DTA (Differential Thermal Analysis) typically operate at heating rates of 2 to 20° C per minute.

As reaction time proceeds, products always continuously evolve towards a mix of higher stability.

The Francis diagram (Figure 1) shows the relative stability of the various alkanes, alkenes and aromatics, on the basis of their tendency to decompose into carbon and hydrogen. All compounds become less stable with rising temperature, except ethyne (acetylene). Alkanes decrease more in stability than alkenes, dienes, and arenes.

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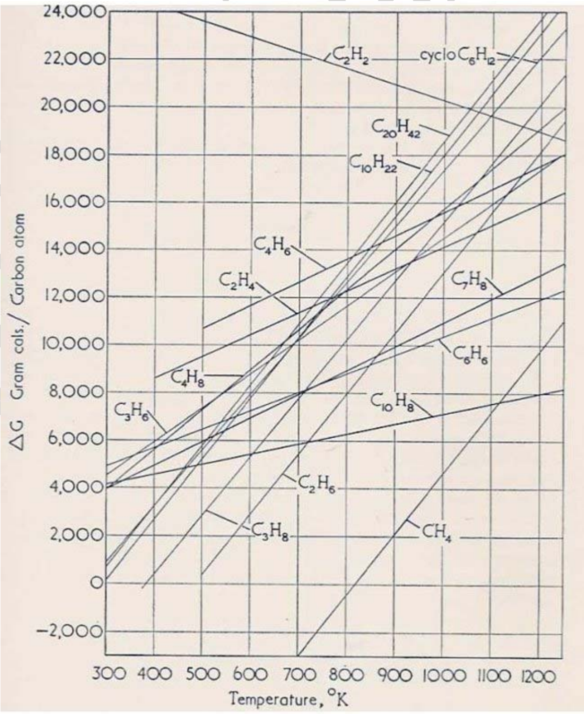

Figure 1: Francis Diagram

1.6. Thermal Decomposition of Inorganic Compounds

Most substances, both organic and inorganic, become unstable when heated, and decompose according to complex and endothermic processes (since chemical bonds are broken), accompanied by rising molar numbers. Examples are:

1) Hydrate Decomposition. Many inorganic compounds are associated with water molecules, at low temperature, e.g. gypsum ($CaSO_4.2H_2O$). When heated gypsum first transforms into hemi-hydrate $CaSO_4.½H_2O$ (at 128° C), then to anhydrite (at 163° C) according to:

$$\underset{\text{Gypsum}}{CaSO_4.2\,H_2O} \rightarrow \underset{\text{Hemi-hydrate}}{CaSO_4.\tfrac{1}{2}H_2O} \qquad (11)$$

$$\underset{\text{Hemi-hydrate}}{CaSO_4.\tfrac{1}{2}H_2O} \rightarrow \underset{\text{anhydrite}}{CaSO_4} \qquad (12)$$

The transition temperature may somewhat differ from equilibrium under actual process circumstances, due to kinetic features of the system.

2) Hydroxide and carbonate decomposition, e.g. hydrated lime (580° C), limestone (897° C):

$$Ca(OH)_2 \rightarrow CaO + H_2O \qquad (13)$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (14)$$

Equilibrium is reached when the partial pressure of evolving volatiles attains atmospheric pressure. In reality, decomposition starts already well below this temperature. Moreover, additives, impurities and possible interactions influence upon actual equilibrium conditions.

3) Sulfate Decomposition proceeds at a higher temperature, e.g.:

$$CaSO_4 \rightarrow CaO + SO_2 + \tfrac{1}{2}O_2 \qquad (15)$$

At ca. 1200° C equilibrium is rapidly attained. Decomposition proceeds earlier, in the presence of carbon or other reducing agents. The above reactions are important in desulfurization.

Thermal behavior of inorganic substances is important in evaluating conditions and properties of combustion residues. At high temperature, most elements appear as oxides. At lower temperatures, however, i.e. in boiler flues, they convert into sulfates, carbonates, chlorides, thus giving rise to reactions inside boiler deposits. These play a role in determining tackiness, hardening of deposits, and corrosion of steam boilers and super heaters.

Many chlorides are volatile, evaporating at flame temperature, and again condensing on

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particulate upon cooling.

2. Combustion Kinetics and Mechanisms

2.1 Survey

Chemical reaction is normally envisaged as the result of colliding molecules that are sufficiently energetic to cause chemical conversion at the molecular scale. Such reactions are elementary, in contrast to those requiring a sequence of chemical steps, such as catalytic or combustion reactions. Chemical mechanisms in combustion involve scores of intermediate reactive species (free radicals) forming at high temperature and again disappearing, once reactions are either completed, or quenched. These species are difficult to monitor during combustion, but their role and reaction rates have been established during dedicated experiments. At present, free radical chemistry is so well established, that complex mechanisms can be simulated with fair precision. Predicting or explaining the heterogeneous processes at the container wall, or that of impurities in the fuel is much more difficult. Both are important in initiating and terminating free radical reactions.

Somewhat similar reaction systems occur in gas phase combustion and pyrolysis, i.e. thermal decomposition in the absence of air. However, combustion is based on oxidation, exothermic, and prone to run-away. Pyrolysis involves the breaking of bonds, is hence endothermic, and controlled by the rate of external heat supply. Numerous aspects of combustion and explosion can only be explained on the basis of complex mechanisms, e.g. the often sharp transition between a seemingly stable situation, involving negligible chemical conversion, and the occurrence of explosion.

A gas phase explosion, i.e. a self-acceleration of combustion has been explained by the thermal and the chemical theory. Semenov developed a simple model for thermal explosions that was later extended by Frank-Kamenetskii.

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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).

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