In this introductory chapter, basic definitions relating to combustion phenomena are provided. A brief discussion of various types of fuels used in practical applications, along with their important characteristics, is presented next. Following this, the possible modes in which combustion can take place, the emissions generated during combustion of fuels and their consequences on environment are discussed.

1.1. Combustion Process – Basic Definitions

Combustion is an exothermic oxidation chemical reaction. In this, a certain quantity of heat is released. The heat release may or may not be accompanied by light emission. In a chemical reaction, there is an exchange of atoms between two reacting molecules as a result of their collision. The number of atoms before and after the reaction remains the same. A combustion reaction involves a *fuel* species and an oxidizer species having distinct characters. These species contain atoms such as C, H, O, N and so on. Commonly used fuel species contain C and H atoms and these are termed hydrocarbons. Commonly used oxidizer species contain O and N atoms. When a fuel species and an oxidizer species are available in sufficient quantities, along with an ignition source, which is a high temperature region, oxidation of the fuel by the oxidizer takes

place. The fuel and the oxidizer are together called *reactants*. As a result of the oxidation process, a set of another species called *product* species are formed and a certain amount of heat is also released. The heat release occurs due to the differences in the energy levels of reactants (having higher energy levels) and the products (having lower energy levels). Depending upon the mode of combustion and type of fuel used, light emission accompanies the heat release.

Examples of fuel species are methane, ethane, ethylene, propane, butane, heptane, benzene, methanol, ethanol, diesel, gasoline, wood, biomass, coal to name a few. Some of these fuels are available in gaseous state under normal temperature and pressure, some are available in liquid form naturally and some in solid state. However, combustion reactions predominantly take place in the gaseous state, even though surface reactions in certain solid fuels are known to take place under certain conditions. Therefore, condensed-phase fuels such as liquid and solid fuels have to be gasified before they can participate in the gas-phase exothermic reactions with an oxidizer. This gasification is called vaporization in the case of liquid fuels and pyrolysis in the case of solid fuels. As gas-phase reactions are very fast, transport processes in the case of gaseous fuels and gasification processes in the case of condensed fuels, control the overall combustion process.

Selection of a fuel for an application depends upon its availability and the cost, apart from its properties. One of the important characteristics of a fuel is its *calorific value*, which is also called the *heating value*. It is the amount of energy that is released when one kg of the fuel is completely burnt and the products are cooled to standard reference temperature (298 K). The amount of fuel to be supplied is determined based on the calorific value of the fuel and the required heat release, usually expressed on a rate basis as the power rating. For this fuel flow rate, sufficient amount of oxidizer should be supplied in order to burn it completely. The most commonly used oxidizer is the atmospheric air, which is available free of cost, unless there is a specific need to use special oxidizers, which are in general more expensive. Before supplying the atmospheric air to the burner, the moisture content and other dusty impurities present in it are removed. For a given mass flow rate of

fuel, a required flow rate of the oxidizer has to be maintained. For example, for 1 kg/s flow rate of methane, at least 17 kg/s of air has to be supplied to ensure almost complete combustion, where it is expected that all the carbon atom in the fuel species are converted to carbon-dioxide and all the hydrogen atoms are converted to water vapor. In most of the burner applications, the nitrogen present in the air behaves almost as a chemically inert species and participates only in the transport of heat. Based on the pressure and temperature of the combustion chamber, the type of transport process that takes place and the environmental conditions, there can be several other products, termed minor products. The usually detected minor products are carbon-monoxide, nitric oxides and unburned hydrocarbons. In a few cases, smoke and soot emission are also possible. These minor products are also called pollutants and it is not desirable to have these in high amounts. There are regulations to restrict the permissible amount of these pollutants that can be produced, depending upon the nature of the application. The accumulation of these pollutants in the atmosphere may be reduced by

- (*a*) controlling the transport processes through a proper design of the burner and the combustion chamber,
- (*b*) controlling the rates of the chemical reactions that produce them using appropriate catalysts and
- (c) by mitigating the harmful effects of the pollutants that are formed using post-combustion devices such as electrostatic precipitators to remove the pollutants before they are released into the atmosphere.

1.2. Types of Fuels and Their Characteristics

As mentioned earlier, fuels exist in gaseous, liquid or solid states under normal atmospheric pressure and temperature. Fuels may further be classified as *fossil* fuels, formed over several years through geological processes and *synthetic* fuels, which are manmade. Commonly available solid fossil fuels are wood, coal and biomass. Naturally available liquid fuel is crude petroleum oil and gaseous fuel is natural gas. These fuels are not available in all regions around the globe. Also, depending on the region of availability, the basic properties of the fossil fuels may be different. For instance, coal available in South Africa, Turkey and India has high ash content when compared to the coal available in the USA or Australia. As mentioned in the previous section, for any fuel, its calorific value, or the heating value, is the primary property that governs the feed rate into a combustion system. In addition, properties such as density (or specific gravity), diffusivity and composition (in the case of multi-component fuels) are important for gaseous fuels or for gasified fuels. Few other properties become important for condensed fuels and these are discussed later.

1.2.1. Gaseous Fuels

Gaseous fuels are more attractive for practical use than condensed fuels since they are cleaner, and devoid of ash and mineral particulates. Hence, they can be directly supplied to the combustion chamber. The design of gas burners and the associated transport phenomenon involved are much simpler, as no gasification, atomization and multi-zone chambers are necessary. However, the main disadvantage of gaseous fuels is their low density and the requirement of large storage space (tanks) for storing sufficient amounts of the fuel for practical applications. This disadvantage may be overcome by storing the gas under high pressure in compressed form or by liquefying and storing it under certain conditions. Even by doing this, depending on the application, the quantity of the gas stored may occupy much higher volume when compared to that of a condensed fuel having the same energy value. Further, high-pressure storage demands thick walled pressure vessels and adequate leak proofing measures, which, if not done properly can cause accidents. A brief look at some commonly used gaseous fuels is presented.

Natural gas is a colorless and odorless gas consisting primarily (around 95% by volume) of methane (CH_4) . Traces of higher order hydrocarbons, carbon-dioxide, water vapor and nitrogen are also usually present in natural gas. Some amount of sulfur may also be present. It is available underground over crude oil deposits. It is extracted, compressed and stored in huge storage tanks. In USA and Europe, natural gas is supplied through pipelines for domestic and industrial usage. It is lighter than air, having a molecular mass

of around 16 kg/kmol, and it has a calorific value between 50000 kJ/kg to 55000 kJ/kg.

Liquid Petroleum Gas (LPG) is a mixture of various hydrocarbons, with butane and propane as its primary constituents. This evolves during refining of petroleum. When the gas mixture is pressurized to over six times the atmospheric pressure, it liquefies. The liquid is stored in steel cylinders and distributed to homes and industries. Once released through a pressure regulator into the atmosphere, the liquid instantly vaporizes into its gaseous components. LPG has a molecular mass of over 50 kg/kmol and is heavier than air. This has the potential to be an explosion hazard as the gas settles down in the event of a leakage. Commercial LPG has a synthetic odorant added for easy leak detection. It has a calorific value between 45000 kJ/kg to 50000 kJ/kg.

Refinery gases are the lighter gases obtained during refining of crude oil. Most of the lighter fractions of the crude oil are converted into gasoline. Other volatile products and lighter gases are extracted as refinery gas. It is a mixture of lighter hydrocarbons, carbon-monoxide and hydrogen. These gases are generally used within the refinery itself.

Coal gas is a derived gaseous fuel. This is obtained during carbonization of certain types of coals. The volatiles, which are gaseous components trapped within the coal, are released during this process. These volatiles primarily constitute the coal gas. Steam is also added in certain carbonization process, which helps in converting some of the carbon in the coal to carbon-monoxide and hydrogen $(C + H_2O \rightarrow CO + H_2)$. Steam also helps in converting *CO* to H_2 via the water-gas shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$. The composition and calorific value of coal gas will vary based on the rank/type of coal used and this is discussed in a later section.

Producer gas is obtained from solid fuels in gas generators. It contains by volume 16-20% of carbon-monoxide, 16-18% of hydrogen and 8-10% of carbon-dioxide, nitrogen and traces of hydrocarbons. Oxygen in the oxidation zone converts C to CO_2 ($C + O_2 \rightarrow CO_2$). This exothermic reaction adds the required heat to the system. When the CO_2 travels through the hot coal layers, CO is formed through $C + CO_2 \rightarrow 2CO$. *Biogas* is obtained from biomass such as vegetable and animal wastes. It contains 60-80% of methane and 20-40% of carbondioxide by volume. Its calorific value lies between 30000 kJ/kg and 32000 kJ/kg. Due to the CO_2 content, the calorific values of producer gas and biogas are lower than natural gas and LPG.

Synthetic gas (or syngas) is produced when solid fuels such as coal and biomass are partially burned in insufficient air (less than that required for complete combustion). It primarily consists of CO and H_2 . Steam is also used to increase the content of hydrogen in the fuel. The calorific value of syngas depends on the calorific value of the solid fuel, type of gasification process and nature of the oxidizer used.

1.2.2. Liquid Fuels

Liquid fuels are advantageous over gaseous fuels as they have much higher energy density. They are better than the commonly used solid fuels such as coal and biomass, as liquid fuels are relatively cleaner and do not leave ash or minerals as products of combustion. However, unlike gaseous fuels, these fuels have to be gasified or vaporized, before they can participate in the combustion reaction. This calls for few additional properties to characterize a liquid fuel, other than its calorific value. The vaporization is dictated by the volatility of the liquid fuel. The volatility is governed by properties such as boiling point, latent heat of vaporization and specific heat. Further, vaporization is a surface phenomenon and surface to volume ratio of the liquid dictates the vaporization rate. To increase the surface to volume ratio, a liquid fuel jet, injected into a combustion chamber, has to be disintegrated into small droplets by a process called *atomization*. The viscosity of the liquid fuel strongly influences the atomization process. Liquids with lower viscosity can be atomized easily. Furthermore, the ignition of the liquid vapor – air mixture is dictated by the flash and fire points of the liquid fuel. It thus becomes clear that several properties are required to characterize a liquid fuel, which have to be estimated and used in design calculations of liquid fuel burners. These are discussed subsequently.

Flash point of a liquid fuel is the minimum temperature of the liquid at which sufficient vapors are produced. The vapor mixes

with atmospheric air and produces a flash or an instantaneous flame, when a pilot flame is introduced over the liquid surface. The flash point corresponds to the formation of an instantaneous premixed flame (formed in properly and already mixed fuel and air) over the fuel surface at a given liquid temperature. When the pilot flame is removed, the flame disappears.

Fire point is a temperature higher than the flash point, at which sufficient vapors are generated. When a pilot ignition source is introduced, a flame is established over the liquid surface and this flame sustains even after the removal of the pilot ignition source. The fire point flame is basically a non-premixed flame, formed around the interface of fuel and air getting mixed in proper proportions.

Boiling point is a temperature higher than the fire point and it is the saturation temperature of the liquid at the given pressure. Liquids with lower boiling points such as gasoline, methanol, n-heptane and so on, vaporize at much rapid rates. Normal boiling point is the saturation temperature at atmospheric pressure. When the liquid reaches its boiling point, there will be no further increase in the temperature as a result of heat addition and all the heat that is added is used to provide the latent heat of vaporization.

The *latent heat of vaporization* is the energy that is required for converting the liquid to its vapor. A higher value of latent heat would indicate that higher amount of heat is required for the phase change at a given pressure and that the liquid may be less volatile.

The liquid fuel is usually at a temperature less than the boiling point to begin with. Heat is required in order to increase its temperature to the boiling point. The heat supplied for this process is termed *sensible heat*. This depends on the specific heat of the liquid. Then for the phase change, the latent heat has to be supplied. Therefore, the volatility of the liquid fuel is generally governed by the liquid-phase specific heat, boiling point and the latent heat of vaporization.

Further, as mentioned above, the viscosity of the liquid plays an important role in the atomization process. In fact, a liquid can qualify as a fuel, only if its viscosity value is within a certain range specified in the standards. Furthermore, one more property that becomes important for a liquid fuel, which is to be used in cold weather, is its *freeze point*.

Liquid fossil fuel, which is usually called *crude oil* or *petroleum*, consists of a large number hydrocarbon compounds, namely, paraffins, isoparaffins, olefins, naphthene and aromatics. Methane, ethane and propane, which are straight chain hydrocarbons are called normal or saturated paraffins. When the number of carbon atoms is more than four, a compound can exist as a normal paraffin, or with a rearranged structure, as an iso-paraffin. Iso-paraffin is an isomer of a normal paraffin. Olefins are unsaturated paraffins. Methene, ethane and pentene are a few examples of olefins. Naphthenes are saturated molecules, with a cyclic or ring structure. Compounds which belong to this category usually have their names prefixed with "cyclo". For example, cyclopentane is a naphthene. Even though its chemical formula is C_5H_{10} , due to its cyclic structure, it is saturated. Finally, aromatics are unstructured molecules with a ring structure. Even though they are unstructured, they are more stable than olefins. Crude oil as a whole has by weight 80% to 85% C, 10% to 15% H and traces of S, O and N for the remaining proportion.

When crude oil is subjected to fractional distillation process, several components are obtained as products. Gasoline, kerosene and diesel are the primary components used in automotive and aerospace industries. Components heavier than diesel cannot be used in these applications unless processed further. These fuels are multi-component in nature and as a result, their density, boiling and freezing points vary across a range. Table 1.1 shows the boiling and freezing ranges of gasoline, kerosene and diesel, as a function of the liquid density.

Fuel	Liquid density @ 20°C (kg/m³)	Boiling point (°C)	Freezing point (°C)
Gasoline	710 to 730	30 to 80	-80 to -60
Kerosene	775 to 810	160 to 200	-60 to -40
Diesel	880 to 900	220 to 280	-50 to -20

 Table 1.1: Boiling and freezing ranges of gasoline, kerosene and diesel

Alternative (non-fossil) liquid fuels are alcohols, liquefied solid fuels and vegetable oils. Ethanol (ethyl-alcohol) is obtained from sources such as sugarcane and corn. Ethanol has characteristics quite similar to gasoline and it may be blended with gasoline and used directly in engines. At present, a 20% - 30% blend of ethanol with gasoline is used worldwide in automobiles. Oils extracted from vegetable seeds such as rapeseed, sun flower seed, neem, jatropha and karanja, have very high viscosity and cannot be directly used in any spray combustion system, where fuels such as gasoline and diesel can be directly used. Therefore, these straight vegetable oils are subjected to a process called transesterification, using alcohols such as methanol or ethanol. By this process, most of their glycerin content is removed and the oils attain the viscosity values that make them suitable for use as a fuel. This processed vegetable oil with much lesser viscosity is called *biodiesel*. Even though biodiesel has a lower calorific value when compared to diesel, its fossil counterpart, its burning characteristics are much cleaner than the diesel; it produces lesser smoke and unburnt hydrocarbon emissions due to the presence of oxygen atoms. At present in unmodified diesel engines, 20% biodiesel – 80% diesel blend can be used to reduce the emissions while retaining the same performance. Bio-derived fuels such as alcohols and biodiesels are renewable in nature and hence may be considered to contribute to green energy. However, issues associated with the sustainability of a biofuel, in terms of growing the required amount of the vegetation for its production, have not been resolved completely.

1.2.3. Solid Fuels

Solid fuels, like liquid fuels, have high energy density. Coal, which is a solid fossil fuel, is available in larger quantities when compared to crude oil, a liquid fossil fuel. Wood, which is a common biomass, has been used extensively as a cheap domestic fuel. However, use of wood as a fuel causes deforestation and burning of wood in primitive stoves under certain conditions can be a health hazard owing to the release of carbon monoxide and smoke arising from incomplete combustion. Coal is of plant origin – formed when vegetation buried underground decays and is subjected to high pressures and temperatures over a period of millions of years. Coal is a high density solid material. It has moisture and gaseous inclusions, which become trapped during its formation. The quality of the coal differs from one location to another based on the degree of completion of the aforementioned formation process.

In general, a solid fuel has *moisture*, gaseous substances called *volatiles*, *fixed carbon* called coke or char and mineral content called *ash*, in some proportions. Proximate analysis is used to determine these fractions. Some solid fuels have sulfur in addition. The calorific value of a solid fuel depends on its volatile and fixed carbon content. The ash content indicates the extent of cleanliness of the solid fuel. A solid fuel is ranked based on its carbon content. Table 1.2 provides the typical mass based percentages of carbon present in solid fuels. These values are calculated based on a moisture-free, ash-free and sulfur-free basis.

Fuel	Fixed carbon %	
Wood	45 – 55	
Peat	50 – 65	
Lignite	60 – 72	
Sub-bituminous	70 – 80	
Bituminous	80 – 90	
Semi-anthracite	90 – 95	
Anthracite	92 – 98	

 Table 1.2: Typical mass based percentages of carbon present in various solid fuels calculated based on moisture-, ash- and sulfur-free basis

The carbon content increases as the formation process nears completion and anthracite, with the highest carbon content of more than 92%, is formed towards the end. The volatile percentage decreases as the fixed carbon content increases in the coal. Volatile content in the coal helps in the ignition process. Carbon burning time is much higher and forms the rate-limiting step in coal combustion. Ultimate analysis is used to precisely determine the chemical composition of the coal. Elements such as C, H, N, S, O and *ash* are determined by this analysis.

Rice husk, wheat husk, saw dust and *wood chips* are a few examples of *renewable biomass* fuels. The availability of some of these fuels is seasonal depending on the amount of the harvest.

These fuels can be processed and used in heating, cooking and local power generation applications. Since the density of these fuels is much lower than coal and wood, these fuels are often pelletized and used as pellets of various shapes. As in the case with liquid biofuels, the sustainability of these solid biofuels is still a matter of uncertainty. In addition to plant derived solid fuels, solid fuels can be obtained from certain animal wastes such as cow dung and can be used locally. Research work has been going on to derive energy from municipal wastes and plastics also.

1.3. Modes of Combustion Processes

As mentioned earlier, combustion reaction occurs with heat release in all cases and along with emission of light of different intensities, in many cases. Modes of combustion can be defined based on the spatial extent where the oxidation reaction occurs. This can be either localized or spread over the entire combustion chamber.

When a fuel is mixed with the oxidizer in proper proportions, the resultant reactant mixture will be *flammable*, which means that when a sufficiently high temperature ignition source is introduced, a combustion reaction will be initiated and sustained in the reactant mixture. When such a flammable reactant mixture is filled in a combustion chamber and a localized ignition source is instantaneously introduced, a combustion reaction involving the reactant mixture can be initiated. Based on the size and configuration of the combustion chamber, a volumetric reaction may occur over the entire chamber almost simultaneously. These types of volumetric reactions occur in small constant volume chambers such as bomb calorimeter, lab-scale constant pressure chambers, well stirred and plug flow reactors. The intensity of the reaction and the speed with which the chain reaction takes place depend upon the boundary conditions, the composition of the reactant mixture and pressure inside the combustion chamber. This can sometimes be so rapid that it is termed an *explosion*. When the reaction chamber is longer (long tube containing reactant mixture) or larger (large spherical vessel containing reactant mixture), the localized ignition source will initiate the reaction only in a small region of the combustion chamber. This localized reaction zone is termed the *flame*. This flame, subsequently propagates through

the combustion chamber, consuming the unburnt reactant mixture. The propagation speed can either be subsonic, which is termed *deflagration*, or supersonic, which is termed *detonation*, based on certain conditions.

On the other hand, when the same reactant mixture is supplied continuously through a *burner* and ignition is initiated at the exit of the burner, a *stationary flame* (non-moving localized reaction zone) may be established near the burner exit, depending on the rate at which the reactant mixture is supplied. These modes of combustion of a flammable reactant mixture occurring without or with a flame are called *premixed combustion* processes. In these modes, the rates of the chemical reaction dictate the flame propagation. The flame propagation speed and its temperature are the important characteristics in a premixed combustion process.

When a fuel alone is supplied to the combustion chamber through one port and the oxidizer alone is supplied to the combustion chamber through another port, transport processes (such as diffusion and convection) occurring in the combustion chamber cause the fuel and the oxidizer to mix. When an ignition source is introduced *instantaneously* at an *appropriate* location, combustion reaction is initiated at locations where the fuel and the oxidizer have mixed in proper proportions. Therefore in such a process, a flame is formed or anchored at certain locations. This flame is called a *non-premixed flame*. Since fuel and oxidizer are supplied through different ports, locations where they are mixed in proper proportion and hence the flame anchoring location(s) will depend (among other things) upon the fuel and oxidizer flow rates. In these situations, the chemical reaction rate is usually very high and the transport processes, which control the mixing of fuel and oxidizer, govern the reaction zones. The extent of the flame, which is governed by the transport processes, is an important characteristic of non-premixed mode of combustion.

Both modes of combustion have their own advantages and shortcomings and are used in many practical applications based on the requirement. This requires a proper understanding of the underlying phenomena leading to a proper design of the combustion chamber/burner.

1.4. Emissions and Environment

Complete combustion of a hydrocarbon fuel results in all the carbon in the fuel being converted to CO_2 and all the hydrogen to water vapor. The overall oxidation reaction that accomplish this takes place in several steps. Breakage of the atomic bonds in fuel and oxidizer species and the formation of intermediate fast reacting species called radicals happen first. The rapid reaction between the radicals and formation of final products happen subsequently. However, due to improper mixing, insufficient residence time and heat and radical losses due to transport processes, the reactions may not proceed to completion in a few regions in the combustion chamber. As a result of this, especially in the case of combustion of heavy fuels, unburnt hydrocarbons, CO and carbonaceous particles, called soot, are released. Even when the reaction is complete, if the temperature of the combustion chamber is high enough, species such as CO_2 and H_2O can dissociate to form CO and H_2 and these may be released to the atmosphere. Since atmospheric air is generally used as the oxidizer, under specific conditions of temperature and pressure, and when sufficient oxygen and residence time are available, nitrogen ceases to be inert and oxides of nitrogen (NO₂) are formed. While burning coal or gasoline, fuelbound sulfur also takes part in the combustion reaction leading to the formation of oxides of sulfur (SO₂). While CO is toxic, unburnt hydrocarbons and soot are carcinogenic. In addition, the nanosized soot particles, when inhaled can lead to respiratory illnesses. The oxides of nitrogen and sulfur, when released into the atmosphere, cause acid rain. This eventually destroys the fertility of the soil. Hence, emissions such as CO, unburnt hydrocarbons, soot, NO, and SO_{x} are harmful to the environment and are appropriately classified as pollutants. Therefore, proper design of the burners and the combustion chamber, which will minimize the production of these emissions to the permissible levels prescribed by emission control boards, is essential.

Although CO_2 has been left out of the list of pollutants mentioned above, it must also be classified as such, since it is a greenhouse gas. In view of this, attempts are being made to develop

mechanisms to capture CO_2 . From an environment prespective, hydrogen alone may be termed a clean fuel, as the main product of its combustion is only water vapor. Although combustion of H_2 with air may produce some amount of NO_x , this may be mitigated by proper design of the combustion chamber. Therefore, fuels with low C to H ratio, such as natural gas and synthetic gas, are desirable as their combustion produces a minimal amount of carbon based emissions.

1.5. Suggested Reading

Towards the end of this book, a list of famous and important text and reference books has been provided. These books have also been referred in the chapters, based on their relevance, by citing their serial numbers within square brackets. Readers may go through the suggested books to get further insight on a particular topic.

Review Questions

- 1. Define combustion.
- 2. What is a fossil fuel?
- 3. What are the pros and cons of a gaseous fuel?
- 4. What is calorific value?
- 5. How flash, fire and boiling points are defined for liquid fuels?
- 6. How does the viscosity of the liquid fuel affect its combustion performance?
- 7. List the types of hydrocarbons present in crude oil.
- 8. How is a solid fuel classified?
- 9. List the advantages and disadvantages of liquid and solid fuels.