Introduction

This book is about combustion science and technology and, as such, covers not only the basic laws and phenomena related to the physics and chemistry of combustion, but also the implications of the fundamental understanding gained therein to the principles behind the practical combustion phenomena affecting our daily lives. It presents the diverse knowledge required of combustion scientists and engineers, the challenges they face, and the satisfaction they derive in providing the proper linkage between the fundamental and the practical.

In Section 0.1 we identify the major areas of practical combustion phenomena, illustrated by some specific problems of interest. In Section 0.2 we discuss the scientific disciplines comprising the study of combustion, and in Section 0.3 we present the classifications of fundamental combustion phenomena. An overview of the text is given in Section 0.4.

0.1. MAJOR AREAS OF COMBUSTION APPLICATION

It is fair to say that the ability to use fire is an important factor in ushering the dawn of civilization. Today our dependence on the service of fire is almost total, from heating and lighting our homes to powering the various modes of transportation vehicles. Useful as it is, fire can also be menacing and sometimes deadly. Wildland and urban fires cause tremendous loss of property and lives every year; the noxious pollutants from automotive and industrial power plants poison the very environment in which we live; and the use of chemical weapons continues to be an agent of destruction with ever greater efficiency. Combustion is certainly one branch of science that affects almost every aspect of human activities.

Practical combustion problems can be roughly divided into the following five major categories, in each of which we cite some examples of current interest.

Energy and Combustion Devices: Despite the large variety of alternate energy sources available, such as nuclear, solar, wind, hydroelectric, geothermal, and OTEC

1

(ocean thermal energy conversion), chemical energy derived from burning fossil fuels supplies a disproportionately large fraction of the total world energy needs—around 85 percent at present. This trend will continue in the foreseeable future because of its convenience, high-energy density, and the economics.

Combustion energy is mainly used to generate heat and power. Examples of this application are domestic heating, firing of industrial furnaces, and the operation of automotive engines and gas turbines. Hence the design and operation of heat and power devices and engines is closely related to the issue of efficient energy utilization. Because of the importance of transportation vehicles as a major consumer of petroleum fuels and contributor of air pollution, there has been extensive development since the early 1970s for more efficient and cleaner burning internal combustion engines for automobiles. For example, the diesel engine offers substantial advantage over the more widely used gasoline engines, for several reasons. First, even though its combustion cycle efficiency is less than that of the gasoline engine for the same compression ratio, it is more efficient overall because it operates at higher compression ratios. Furthermore, unlike the gasoline engine, which requires highly refined fuels with narrow specifications, the diesel engine is very fuel tolerant. Thus diesel fuel requires less refining than gasoline and, consequently, results in a net saving in processing energy at the refinery stage. This property of fuel tolerance also implies that the diesel engine is a good candidate for the use of unconventional or low-grade fuels. The diesel engine, however, does have the potential disadvantages of being relatively noisier and a heavy emitter of soot and oxides of nitrogen (NO_x); both problems have their origin in its operational principle and therefore require fundamental combustion research. It is nevertheless gratifying to note that much progress has been made recently in alleviating these problems.

An important concept in engine development is that of stratified charge combustion. The basic idea is that the combustion of lean mixtures has the potential of simultaneously increasing the combustion efficiency and reducing the formation of most pollutants. Lean mixtures, however, are hard to ignite. Therefore, the concept of stratified charge combustion is to stratify an overall fuel lean mixture from relatively rich to ultra lean. Since the relatively rich portion can be ignited easier, the hot combustion products so generated can in turn ignite the ultra lean portion of the charge. Thus by combining the merits of high-pressure combustion, direct fuel injection for uniform cylinder-to-cylinder charge distribution and controlled fuel vaporization, spark ignition for controlled ignition event, and stratified charge combustion, there has been considerable development on high-compression-ratio, direct-injection, spark-assisted, stratified charge engines.

In contrast to stratified charge engines, there is also considerable interest in the development of HCCI (homogeneous charge compression ignition) engines. Conceptually, by having reaction taking place homogeneously within the entire engine cylinder, instead of being confined to localized, high-temperature regions constituting the flames, the formation of soot and NO_x can be substantially reduced.

Furthermore, higher compression ratios and hence higher efficiency can be attained with compression ignition.

The fact that improvements in the engine performance can be pursued through the opposite concepts of stratified and homogeneous charges not only demonstrates the complexity of the combustion phenomena underlying such technological processes, but it also highlights the richness of the possible avenues that can be explored for optimization.

Fuels: Combustion needs fuel. Furthermore, the satisfactory operation of different heat and power engines usually depends critically on the compatibility of the fuel used. Examples are the unsuitability of diesel fuel for use in gasoline engines because it is relatively less volatile, and the narrow compositional specifications of gases which can be used in domestic gas stoves in order to maintain flame stabilization by avoiding blowoff and flashback.

The importance of fuel in combustion has been receiving increased interest because of the concern over the shortage and reliability of petroleum supply. Thus "energy crisis" is simply a "fuel crises." Since the world's petroleum supply is projected to be severely depleted within this century, the long term solution for the next few centuries in terms of fossil fuels appears to largely depend on the burning of coal, either through direct utilization or as coal-derived fuels. Two approaches for direct coal utilization are being actively pursued. The first is fluidized-bed combustion, in which air is introduced through the bottom of a bed of coal particles at a sufficiently fast rate such that the particles are levitated, that is, fluidized. This approach has the advantages that the coal particles are in direct contact with the oxidizing air such that their burning rates are maximized, that neutralization of oxides of sulfur (SO_x) can be facilitated by mixing limestone with the coal particles, and that the production of NO_x can be minimized by controlling the fluidization rate. The second approach for direct coal utilization is the burning of coal–water slurries. Here, finely crushed coal particles of sizes ranging between 40–70 μm are mixed in water and sprayed directly into the combustion chamber of industrial furnaces. The advantages are that the physical processes of coal crushing and mixing are less energy expensive than the chemical process of coal liquefaction, and that the slurries can be transported through pipelines and subsequently directly burned in conventional oil-fired combustors. This requires minimum hardware modification, and thereby capital outlay and combustor downtime. Slurries up to 70 percent coal content have been successfully burned.

Oil can also be derived from coal. These coal-derived oils have higher boiling points, wider boiling point ranges, and higher contents of aromatics and nitrogen-containing compounds. Consequently, they tend to produce more soot and NO_x. Various alternate and hybrid fuels have also been formulated. Prominent among these are methanol, ethanol, and mixtures of ethanol with oil. Methanol can be derived from natural gas and coal, while both methanol and ethanol can be produced

from biomass. Alcohols have smaller heats of combustion because of the extra oxygen atom in the molecule. However, they have higher knock ratings in gasoline engines and produce less NO_x and soot. Blends of ethanol and gasoline, and methanol and gasoline, have been successfully marketed.

Coal, of course, can also be gasified in the presence of air, with or without steam, to produce a combustible gaseous fuel that consists of hydrogen and carbon monoxide. Coal gasification becomes progressively more attractive as a source of clean fuel with the dwindling supply of natural gas.

Pollution and Health: The major pollutants from combustion are soot, SO_x, NO_x, unburned hydrocarbons (UHC), and carbon monoxide (CO). As just mentioned, soot is expected to be a serious problem with the burning of coal-derived fuels and the large-scale deployment of high-compression engines such as the diesel. Soot not only is unsightly but can also be carcinogenic due to the condensation and thereby presence of carcinogenic liquid combustion products on the particle surface.

The main source of SO_x is from burning coal. When combined with water in the atmosphere, the emitted SO_x forms sulfuric acid and precipitates as acid rain, with devastating effects on aquatic life and soil erosion.

NO_x can be formed from either the N_2 in the atmosphere or the nitrogen atoms in the fuel molecules, with the former produced under high-temperature, intense combustion situations because of the need to dissociate the nominally inert N_2 in the air. Fuel-bound NO_x is less temperature sensitive and could be a major contributor of NO_x emission from burning coal or coal-derived oils. When it reacts with UHC and ozone in the presence of sunlight, NO_x forms smog that is detrimental to the respiratory system.

A problem of potential concern is indoor pollution. With houses being better insulated to conserve energy, the trace pollutants (CO, NO_x, UHC), from such domestic heating devices as the gas stove, furnace, and kerosene heater, may exist at sufficiently high levels as to be injurious to health.

There is also interest in applying combustion technology in the management of municipal, munition, and chemical hazardous wastes through incineration. The problems with burning these wastes are the uncertainty of the toxicity of the combustion intermediates and products and the fact that some of the chemicals are halogenated compounds, which can be resistant to efficient burning because of the scavenging of the crucial hydrogen atom by the halogen radicals in the oxidation process.

A serious, and potentially catastrophic, environmental problem is global warming caused by the increased amount of anthropogenic CO_2 in the atmosphere. Since CO_2 is a by-product of hydrocarbon combustion, suggestions have been made to use hydrogen as the primary fuel source. In the event that hydrogen is derived through the conversion of hydrocarbons, CO_2 is still produced during conversion and needs to be sequestered properly in order to prevent its release into the atmosphere.

A discussion on the adverse effects of combustion on health would not be complete without mentioning the well-established cancer-causing consequence of cigarette

smoking, which is simply the slow combustion of tobacco leaves. The knowledge of combustion science has not been sufficiently brought to bear on this problem of immense importance.

Safety: This topic can be divided into three categories, namely fires, explosions, and materials. Fires, both structural and wildland, are costly in terms of human suffering as well as financial loss. Problems of interest include improving fire detection technology and understanding the dynamics of fire propagation in confined spaces such as buildings and aircraft cabins.

Explosions are of concern to safety in mine galleries and grain elevators, as a consequence of LNG (liquefied natural gas) spills or rupturing of pressurized hydrogen storage tanks in urban areas, and in nuclear reactor accidents. In the last example, hydrogen gas is generated and could accumulate in sufficient quantity to cause an explosion. This would in turn rupture the reactor containment structure, causing the release of radioactive gases into the environment.

Since the inhalation of smoke and the toxic products of combustion is a cause of fatality in fires, the choice of materials for structure and decoration is also an important consideration in the overall strategy for fire control.

A strategy toward the prevention of fires and explosions in aircraft and combat vehicles, such as tanks, is the development of fire-safe fuels which, while burning well within the engine, will not catch fire upon spillage. For example, diesel oil emulsified with a small amount of water has been found to be fire resistant.

Defense and Space: The various defense establishments are interested in the formulation of high-energy munitions and propellants; the suppression of combustion instability within jet engines, rockets and guns; signature and detection vulnerability from the exhausts of jet engines and rockets; and measures at preventing explosion of fuel tanks when being penetrated by projectiles. The development of chemical lasers as an intense power source and of hypersonic aircraft up to Mach 25 are also of interest to the national defense.

Since combustion experiments conducted on earth are frequently complicated by the presence of buoyant flows, there has been much interest to conduct these experiments in the weightless environment of a space shuttle or station. The intrusion of buoyancy is particularly problematic when the burning is slow as in the propagation of a flame in a weak mixture, or for long-duration phenomena such as smoldering. The presence of buoyancy can also distort the flame configuration from an otherwise symmetrical one, and hence significantly complicates data reduction as well as theoretical analysis or computational simulation of the phenomenon of interest.

Fire safety is of paramount interest in space exploration. For example, while earthbound smoke detectors of incipient fires are placed at the ceiling of a room in order to capture the buoyancy-driven, upwardly rising smoke, they are clearly inoperative in the weightless space environment. Furthermore, flammability standards

established on earth may not have much meaning for the fire safety evaluation of a spacecraft.

Recognizing that the environment within a space craft is artificial anyway, there has been the suggestion of creating an almost fire-proof living environment so that fire hazard ceases to be a concern. This concept is based on the recognition that whereas ignition and combustion intensity depend on the fractional amount of oxygen in the oxidizing gas, human comfort depends only on the absolute amount of oxygen. Furthermore, it is also empirically known that the combustibility of most organic materials decreases drastically with decreasing oxygen concentration. They become hardly flammable when the oxygen concentration is reduced to less than, say, 15 mole percent. Thus if we can reduce the cabin oxygen concentration to half of its value in air, but increase the cabin pressure to two atmospheres, then a comfortable, but fire-proof environment can be created.

0.2. SCIENTIFIC DISCIPLINES COMPRISING COMBUSTION

Combustion is the study of chemically reacting flows with rapid, highly exothermic reactions. It is interdisciplinary in nature, comprising thermodynamics, chemical kinetics, fluid mechanics, and transport phenomena, each of which has the following roles.

Thermodynamics: In combustion processes reactants are converted to products, releasing heat for utilization. The science of thermodynamics allows us to do the bookkeeping on how much chemical energy is converted to thermal energy in such a process, and to determine the thermal and compositional properties of the products when equilibrium is reached. The laws of equilibrium thermodynamics are firmly established, although the thermodynamic properties of many of the reacting species, including large and complex fuels and their reaction intermediates, are still not well determined.

Chemical Kinetics: While thermodynamics links the initial state to the final, equilibrium, state of a reactive mixture, it does not tell us through which path, and for how long, such a transformation takes place. For example, if a particular reaction requires more than an hour to proceed to near completion, we obviously need not take it into consideration when analyzing the cycle performance of an automotive engine. In fact, conclusions based on such equilibrium calculations could be quite erroneous. An example is the calculation of NO_x emission from engines—calculated amounts of NO_x emission based on finite reaction rates far exceed those determined by assuming thermodynamic equilibrium at the exhaust temperature. Since all combustion processes have some finite, characteristic times defining the relevant phenomena, chemical kinetics is needed to prescribe the paths and rates through which reactions take place during such times.

Chemical kinetics is a complex subject, especially for combustion systems in which a myriad of chemical species exist, each of which has the potential of interacting with

the rest. As an illustration of its complexity, it may be noted that, at present, only the oxidation mechanisms of such simple fuels as hydrogen and methane can be considered to be reasonably well understood to allow for the prediction of such global combustion characteristic as the burning rate of a laminar flame, provided the pressure is not too high.

Fluid Mechanics: Since the combustion systems we are interested in frequently involve chemical reactions occurring in a flowing medium, knowledge of fluid mechanics is an essential prerequisite for a successful understanding of many combustion phenomena. Here combustion distinguishes itself from being merely a branch of chemistry in that it is chemistry and more. By the same token, a fluid dynamicist cannot satisfactorily describe a combusting flow field without paying adequate attention to the effects of chemical reactions. As an example, the highly localized and exothermic nature of chemical reactions causes significant temperature, and therefore density, variations in a flow, implying that the frequently invoked assumption of constant density in fluid mechanics can be a rather poor one in combustion studies.

Both chemical kinetics and fluid mechanics are major scientific disciplines by themselves. When coupled through combustion, the complexity and richness of the resulting phenomena take on a new dimension, as we shall demonstrate throughout this text.

Transport Phenomena: As just mentioned, in a combustion flow field the chemical reactions frequently occur in highly localized regions of reaction fronts, which are characterized by high temperatures, high product concentrations, and low reactant concentrations. On the other hand, in regions away from these reaction fronts, the temperatures and product concentrations are low while the reactant concentrations are high. The existence of these temperature and concentration gradients will cause the transfer of energy and mass from regions of high values to regions of low values through the molecular process of diffusion. For heat transfer, radiation can also be important. Mechanistically, the existence of diffusive transport is crucial in the sustenance of many types of flames in that it is only through these processes that fresh reactants can be continuously supplied to the flame, while the heat generated there is also being continuously conducted away to heat up and thereby cause ignition of the fresh mixture. Since a reaction can proceed only when its participating species can be brought to the neighborhood of a physical location and remain there for a period of time sufficiently long for the reaction to consummate, strong coupling between transport and chemical kinetics in determining the local reaction rate is to be expected.

0.3. CLASSIFICATIONS OF FUNDAMENTAL COMBUSTION PHENOMENA

In this section, we introduce the various classifications of fundamental combustion phenomena and the terminology usually associated with them.

Premixed versus Nonpremixed Combustion: This is probably the most important classification of combustion phenomena. At the global level, a combustion system frequently consists of two reactants: a fuel and an oxidizer. These two reactants must be brought together and mixed at the molecular level before reaction can take place, as just mentioned. Therefore, the mechanisms of mixing are essential elements in influencing combustion. The requirement of mixedness also implies that at least one of the reactants should be in either the gaseous or the liquid phase so that its molecules can "spread around" those of the other reactant.

Because of the importance of molecular mixedness, combustion systems behave quite differently depending on whether the reactants are initially mixed or not. In a premixed system, the reactants are already well mixed before reaction is initiated. However, in a nonpremixed system the reactants are initially separated and are brought together, through the molecular process of diffusion and the bulk convective motion, to a common region where mixing and subsequently reaction take place. Nonpremixed combustion is also known as "diffusion combustion" because diffusive transport is essential in effecting mixing of the reactants at the molecular level. It is, however, important to recognize that by calling a nonpremixed system diffusional does not imply a premixed system is nondiffusional. The word "diffusional" only indicates the need to bring the reactants together via this transport mechanism. In a premixed system, diffusion is still needed to transport the premixture to—and the thermal energy and the combustion products away from—the reaction region where the reactants are consumed and the thermal energy and combustion products generated.

A Bunsen flame, shown in Figure 0.3.1, provides an illustration of both types of flames. Here as the fuel gas issues from the fuel orifice, air is entrained through the adjustable air intake port and is then mixed with the fuel gas as they travel along the burner tube. The subsequent reaction between the fuel and oxygen in this mixture forms a premixed flame. Assuming that the air flow rate can be manipulated, then the resulting flame can be either fuel rich or fuel lean depending on whether the oxygen or fuel can be completely consumed. If this mixture is fuel lean, then the excess oxygen will remain unreacted after passing through the flame and will be "exhausted" to the environment. However, if it is fuel rich, then after passing through the premixed flame the excess fuel, or rather the fuel-related intermediate species, can further react with oxygen in the ambient air. Since oxygen and the fuel species are initially separated, they need to be transported to a common region where mixing and reactions occur. This results in a nonpremixed flame, at which the outwardly directed fuel species react almost completely with the inwardly directed oxygen. The entire flame ensemble therefore consists of a premixed flame and a nonpremixed flame. Finally, in the event when the air intake port is completely closed, then the burner mixture does not contain any oxygen and, as such, only the nonpremixed flame exists.

It is obvious that one would not find many examples of premixtures in nature because they would have already reacted even if they are only slightly reactive. On
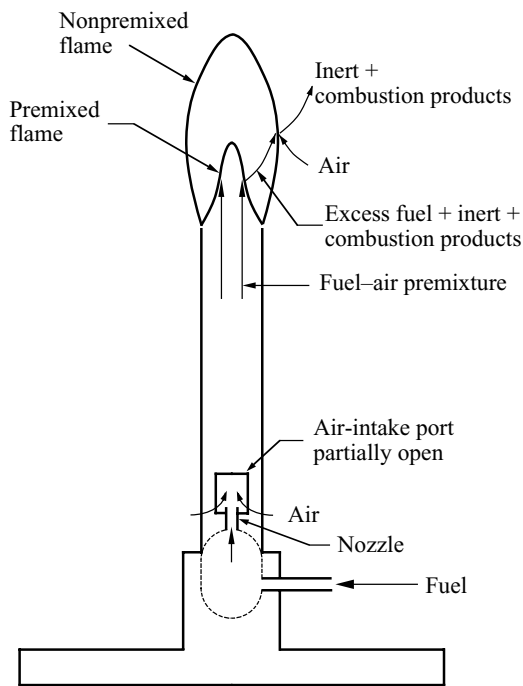
Figure 0.3.1. Schematic of the Bunsen flame.

the other hand, nonpremixed systems abound. Indeed with oxygen in the air as the oxidizer, then all materials that can burn in air are fuels. Examples are fossil deposits such as petroleum and coal, cellulosic materials such as paper and cloth, and metallic substances such as aluminum and magnesium.

Laminar versus Turbulent Combustion: A flame is also characterized by the nature of the flow, whether it is laminar or turbulent. In a laminar flow distinct streamlines exist for the bulk, convective motion, whereas in a turbulent flow such streamlines do not exist such that at any point in space the flow quantities randomly fluctuate in time. The existence of turbulence generally facilitates the coarse mixing process, and therefore has a particularly strong influence on nonpremixed systems in which reactant mixing is essential. The final mixing before reaction can take place, however, must still occur through the molecular diffusion process whether the flow is laminar or turbulent.

Subsonic versus Supersonic Combustion: A second way to characterize combustion according to the nature of the flow is the velocity of the flow, whether it is subsonic or supersonic. In a subsonic flow, the molecular collision processes of diffusion are predominant while reactions also have more time to complete. These are the flames we encounter most frequently in our daily lives, such as the candle flame and the pilot flame. In supersonic combustion the high flow velocity usually renders convective transport to dominate diffusive transport. Reactions also have less time to proceed.

Wave motions involving shocks and rarefactions are likely to be present. Supersonic combustion is usually associated with explosions and supersonic flights.

Homogeneous versus Heterogeneous Combustion: This is among the most confusing terminology in combustion literature. Traditionally, a combustion phenomenon is called homogeneous if both reactants initially exist in the same fluid phase, either gas or liquid. An example is the Bunsen flame just discussed. If the two reactants initially exist in different phases, whether gas–liquid, liquid–solid, or solid–gas, then the combustion is heterogeneous. An example is a coal particle burning in air.

On the other hand, chemists define a heterogeneous reaction as one in which the reactants actually exist in different phases at the location where reaction takes place. Therefore, in the case of coal burning in air, the reaction is heterogeneous when the solid carbon in the coal reacts with the oxygen from air at the particle surface. However, the reaction is homogeneous when there is substantial devolatalization such that the outgassing fuel vapor reacts with oxygen in the gas phase. According to the conventional combustion definition, both modes of burning are called heterogeneous combustion.

Homogeneous-versus-heterogeneous combustion is sometimes also used to designate the uniformity of the mixture. Thus a process is called homogeneous when there is no temperature or concentration gradient in the mixture. An example is the (homogeneous) explosion of a uniform mixture of fuel and air, as in the HCCI engine mentioned earlier. However, if combustion occurs in a gaseous mixture containing fuel vapor pockets produced through, say, vaporization of fuel droplets, then the process is sometimes called heterogeneous.

In order to avoid confusion, we shall be as specific as possible in describing different phenomena. For example, the reaction between vaporized fuel from a coal particle and air will be called "gas-phase reaction," while the reaction between oxygen and solid carbon at the particle surface will be called "surface reaction." This circumvents the uncertainty in designating the former as either a heterogeneous or homogeneous reaction.

0.4. ORGANIZATION OF THE TEXT

The present text aims to give a fairly comprehensive treatment of fundamental combustion phenomena. The next four chapters provide the physical and chemical fundamentals needed to describe combustion processes. Specifically, Chapter 1 discusses equilibrium thermodynamics, which relates the initial and final states of a chemically reacting, multicomponent thermodynamic system, culminating in the calculation of the adiabatic flame temperature. Chapter 2 introduces the general concepts of chemical kinetics and Chapter 3 studies the reaction mechanisms of some practical fuels. Together, these two chapters provide a fairly comprehensive introductory coverage of the chemical aspects of combustion, leading to an appreciation of the complexity of the reaction mechanisms governing hydrocarbon oxidation. In Chapter 4, we study