1

Introduction to Combustion

1.1 Introduction

The goal of this book is to provide insight into the modeling and analysis of combustion processes. The term combustion encompasses many high-temperature chemical reactions that involve oxygen. Combustion is a chemical reaction between a fuel and an oxidizer producing heat and light. It is a rapid energy conversion process that converts molecular energy stored in the fuel to thermal energy. The book covers the basic principles of combustion with a focus on the application of the chemical and thermal sciences to better understand combustion processes.

Our society relies heavily on the thermal energy released by combustion to meet a wide variety of needs, as most (~85%) of the world's energy use comes from combustion processes. This energy from combustion is primarily used for three purposes: to supply heat, to provide power, and to produce manufactured materials. We use petroleum in the form of gasoline, diesel, or kerosene for transportation, natural gas for heating our buildings and industrial processes, and coal and natural gas for electricity generation.

The mix of U.S. energy production and consumption has changed over time. Fossil fuels have dominated the U.S. energy mix for more than 100 years, but the mix has changed. Currently, in 2023, about a third of the U.S. energy production is petroleum based and another third is natural gas, with the remaining third a combination of renewables, coal, and nuclear energy (Smil 2017).

There are a number of private and governmental initiatives underway to decarbonize, i.e., reduce the amount of greenhouse gas emissions, primarily CO_2, from combustion devices. About three-quarters of the worldwide greenhouse gas emissions are due to the combustion of fossil fuels. The goal of decarbonization is to limit global warming to no more than 2.0 °C by 2050. The initiatives include increased use of biofuels and carbon-free fuels such as hydrogen and ammonia and improved combustion and process efficiency. Two technologies have dominated policy discussions about mitigating climate change: renewable energy generation and carbon capture and storage. Renewable technologies for electricity generation now being deployed widely are wind turbines and solar cells. Carbon capture and storage technologies include a process of converting carbon dioxide into fuel. In a two-stage process, the CO_2 gas is chemically captured and turned into a solid form as calcium carbonate, then heated to drive off the CO_2 and convert it to carbon monoxide.

Principles of Combustion, Third Edition. Allan T. Kirkpatrick and Kenneth K. Kuo.

Companion website: www.wiley.com/go/kirkpatrick/principlesofcombustion3e

1.2 Combustion Applications

Electrical power generation: Natural gas and coal are burned in the furnaces of electrical power stations to produce steam in order to generate electricity. For many years, most power plants used coal as a fuel, but due to health, economic, and climate change considerations, coal is being replaced by natural gas and also renewable energy sources.

Transportation: Liquid and gaseous fuels are used as an energy source for transportation by automobiles, trucks, aircraft, and ships due to their high energy density. Gasoline and diesel fuels are the major fuels used in internal combustion engines, and kerosene and natural gas are the major fuels used in gas turbines. There have been significant developments since the late 1960s in internal combustion engine and gas turbine technology in order to reduce their emissions and increase thermal efficiency.

Process industry for materials manufacturing: Manufacturers of primary metals (iron and steel), nonferrous materials (glass, ceramics, cement, and nanoparticles), chemicals, petroleum products, food, and paper produce these materials through heating and combustion processes. The combustion devices used in materials manufacturing include boilers, furnaces, ovens, and blast furnaces. For example, cement is produced by sintering ground limestone to 1450 °C in large kilns. In the Haber process, hydrogen and nitrogen are reacted together at high temperatures and pressures to produce ammonia, NH_3.

Domestic and industrial heating: Heating of residential homes, commercial buildings, industrial factories, offices, and various types of buildings such as schools and hospitals is accomplished through combustion of natural gas. There is an extensive natural gas network in the United States and many countries which delivers natural gas directly to a domestic and industrial end user.

Cooking More than 2.5 billion people, about 1/3 of the world's population, rely on solid biomass, kerosene, or coal as their primary cooking fuel. The burning of solid fuels in households for cooking and heating can lead to very low indoor air quality and health issues.

1.3 Organization of Text

In Chapter 1, we introduce various applications of combustion processes, fuels, and emissions from various combustion applications. As discussed below, these applications include electrical power generation, transportation, industrial processes, and heating of domestic and commercial buildings. The major fuels for these combustion processes include natural gas, liquid hydrocarbons (gasoline and diesel fuels), and solids (wood and coal).

Chapter 2 covers chemical thermodynamics, including thermodynamic properties of fuel–air mixtures and equilibrium thermodynamics of multicomponent reacting systems. Chapter 3 reviews chemical kinetics, reaction rates, and the rate of production of combustion products. Chapter 4 introduces detailed reaction mechanisms of various fuels. In Chapter 5, the general conservation equations of mass, momentum, energy, and species for reacting systems are presented. Chapter 5 also introduces turbulence models and turbulent combustion.

In Chapter 6, premixed laminar flames are modeled to determine burning velocities and flammability limits. Chapter 7 examines subsonic deflagration waves and supersonic detonation waves of premixed gases. Chapter 8 covers non-premixed or diffusion flames, including jet mixing and flame length. In Chapter 9, the evaporation and burning of fuel droplets are presented. Chapter 10 discusses the emissions, including nitrogen oxides, carbon monoxide, carbon dioxide, and particulates from combustion processes. The final chapter, Chapter 11, introduces the processes

of solid fuel (biomass, i.e., wood and coal) combustion. A Homework Problem section is included at the end of each chapter.

1.4 Solution Methods for Combustion Problems

A combustion problem can be solved using various combinations of analytical, computational, and experimental approaches. The text introduces a number of solution techniques and gives background references for more information. Although the design of many modern combustion systems leans toward calculation and simulation rather than extensive hardware fabrication and testing, diagnostic techniques are still very important.

Indeed, the rise in computational fluid dynamics (CFD) is beginning to allow the evaluation of complex flow and combustion systems over a wide range of design parameters more quickly, inexpensively, and thoroughly than can be accomplished with actual hardware tests. Reactive flows including multistep kinetic considerations have become computationally tractable. For example, there are three major categories of numerical analysis, Reynolds average Navier–Stokes (RANS), large-eddy simulation (LES), and direct numerical simulation (DNS). The predictions of these numerical solution techniques for a diffusion flame are shown in Figure 1.1. A discussion of these methods is provided in Chapter 5.

However, these computational models often require adequate input of kinetic information in the form of sub-models, which are based on specific measurements or basic understanding of the chemical and physical mechanisms derived from experimental observations. In particular, experimental validation of computed results will be necessary to prove the predictive capability of theoretical models and computer codes before they are used for guiding actual designs.

There are a number of software packages available for numerical solution of combustion problems, from commercial, national laboratory, and academic sources. A popular open-source program is Cantera, which is a suite of software tools for problems involving chemical kinetics, thermodynamics, and transport processes. Since Cantera is open source, users can incorporate detailed chemical kinetics and transport models into their calculations. Cantera can be used from Python and Matlab, or in applications written in C/C++ and Fortran 90.

A popular commercial combustion software tool is Chemkin-Pro. Many researchers work with combustion mechanisms in Chemkin format, which has become a de facto standard in

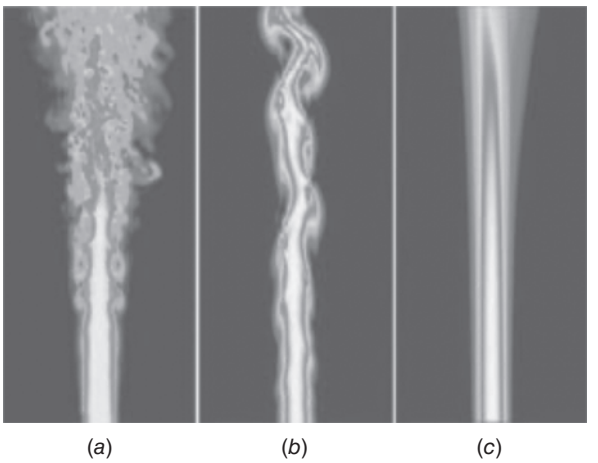


Figure 1.1 Predicted results for a diffusion flame using (*a*) DNS, (*b*) LES, and (*c*) RANS. (Courtesy of Prof. P. Givi.)

the combustion community. The Chemkin software was originally developed in the U.S. Sandia National Laboratories and has since become a standard computational program for combustion engineering as well as in other fields such as fluid dynamics and chemistry. The Chemkin-Pro package is a set of programs which incorporate complex chemical kinetics into simulations of gas-phase and gas-surface reacting flow. The software includes application programs for stirred reactors, plug-flow reactors, premixed and diffusion flames, and opposed-flow diffusion flames. For specific applications such as combustion in internal combustion engines and gas turbines, commercial software packages such as Converge, WAVE, OpenFOAM, Fluent, STAR-CD, and KIVA are also used by the combustion research community.

1.5 Fuels Background

In this and the next few sections, we introduce a range of conventional and alternative fuels used in combustion devices. We discuss the chemical structure of fuels and oxidizers, their thermodynamic properties, and their use in various combustion devices, such as boilers, internal combustion engines, gas turbines, and rockets.

A typical hydrocarbon-based liquid fuel may consist of 100 different hydrocarbons and another 100–200 trace species. Gasoline and diesel fuels are primarily obtained by distillation from petroleum oil. Petroleum oil has a relatively low cost and a high energy density. Since petroleum contains carbon, its combustion produces carbon dioxide, a greenhouse gas contributing to global warming and climate change.

Petroleum is a fossil fuel composed from ancient organic materials. Formation of petroleum and natural gas reservoirs occurs underground during the pyrolysis of hydrocarbons in a variety of endothermic reactions at high temperature and/or pressure. Wells are drilled into oil reservoirs to extract the crude oil. In 1858, Edwin Drake drilled the first U.S. oil well, a 21-m deep well in Titusville, Pennsylvania. He is credited with inventing the technique of drilling inside a pipe casing to prevent water seepage. Innovations in the technology for oil recovery have allowed deeper and deeper wells to be drilled, both on land and in the oceans. In Europe, petroleum oil is currently extracted from reservoirs located about 3000 m below the North Sea seabed.

The identified worldwide crude oil reserves are estimated by the American Petroleum Institute to be about 1 trillion barrels, with 0.6 trillion barrels remaining to be identified. At present consumption rates, at about 100 million barrels per day, it is estimated that petroleum reserves will last for 60–95 years. Technological advances in extraction have created continual increases in the size of the worldwide petroleum reserves. In 1950, the identified worldwide petroleum reserves were estimated to be about 0.09 trillion barrels, so in the last 60 years, the identified petroleum reserves have increased 10-fold. To put the consumption of petroleum into perspective, about 0.7 trillion barrels of petroleum have been consumed since the advent of the Industrial Revolution. The recent invention and commercialization of hydraulic fracturing, commonly known as “fracking,” have enabled greater production of petroleum and natural gas from shale and related geological formations.

Crude oil is classified by its geographical origin, its American Petroleum Institute (API) gravity (light, heavy), and its sulfur content (low sulfur is labeled as sweet, and high sulfur is labeled as sour). Light crude oil produces a higher gasoline fraction. Sweet crude oil is more valuable than sour crude oil because it requires less refining to meet sulfur standards. Crude oil contains a very large number of different hydrocarbons. For example, 25,000 different compounds have been found in one sample of petroleum-derived crude oil. The compounds range from gases to viscous liquids and waxes.

Solid fuels like wood and coal are heterogenous hydrocarbon compounds that do not burn completely. Their combustion residue is in the form of inorganic ash particles. Gasification is a combustion technique that has been developed to convert a solid fuel into a clean gaseous fuel that can be used in combustion devices. Coal and woody biomass are broken down at high temperature (between 700 and 800 °C) and high pressure in a low-oxygen environment, a process called pyrolysis. Coal and wood gasification has many applications, as it has been used for the generation of synthetic natural gas ("syngas"), hydrogen, ammonia, and specialty chemicals.

A gasifier differs from a typical combustor as it uses a controlled air or oxygen supply and steam. With coal or wood gasification, only drying, distillation, and pyrolysis processes occur. The pyrolysis reactions are controlled by the level of oxygen or air made available for the reactions. A volatile flame is not established. The products are low molecular mass hydrocarbons, CO, H_2, CO_2, H_2O, N_2, and tar. The tar, char, and ash particles and any vaporized inorganic compounds are filtered from the pyrolysis products before use in an engine.

Coal gas was the primary source of gaseous fuel in the United States until replaced by natural gas in the 1940s. Coal gas is obtained by coking, i.e., partial pyrolysis of coal, similar to the process of producing charcoal from wood. The pyrolysis process drives off the volatile constituents in the coal. Coal gas is typically 50% hydrogen, 35% methane, 10% carbon monoxide, and other trace gases such as ethylene. The earliest internal combustion engines in the late 1800s were fueled with coal gas.

Biogas, a mixture of methane and carbon dioxide, is produced from the decay of organic matter. When organic matter, such as kitchen scraps and farm or livestock waste, decays anaerobically at low temperature with no oxygen present, either in nature or under controlled conditions in a sealed tank, it ferments, producing biogas. Feedstocks can include residues from the harvest of wheat, maize, rice, sugar beet, sugar cane, soybean, and other crops. The methane content of biogas typically ranges from 45% to 75% by volume, with most of the remainder being CO_2. The Assyrians may have used biogas to heat bath water, and Marco Polo reported that in the 13th century, the Chinese extracted energy from covered sewage pots. Biogas from sewage treatment powered English streetlights in the 1890s. In the United States, the primary pathway for biogas has been through landfill gas collection.

1.6 Hydrocarbon Fuel Chemistry

Hydrocarbon fuels are composed of blends of hydrocarbons, grouped into families of hydrocarbon molecules termed paraffins, olefins, naphthenes, and aromatics. The hydrocarbon families each have characteristic carbon–hydrogen bond structures and chemical formulae.

Paraffins (alkanes) are molecules in which carbon atoms are chained together by single bonds. The remaining bonds are with hydrogen. They are called saturated hydrocarbons because there are no double or triple bonds. The general formula for the paraffin family is $C_nH_{(2n+2)}$. The number of carbon atoms is specified by a prefix:

1-meth	2-eth	3-prop	4-but
5-pent	6-hex	7-hept	8-oct
9-non	10-dec	11-undec	12-dodec

Paraffin is designated as an alkane by the suffix *-ane*. Examples of paraffins are methane, CH_4, and octane, C_8H_{18}, as shown schematically in Figure 1.2. Compounds with straight chains are also labeled as normal or *n*-. Octane is sometimes called normal octane or *n*-octane, and straight-chain heptane, C_7H_{16}, is labeled *n*-heptane.

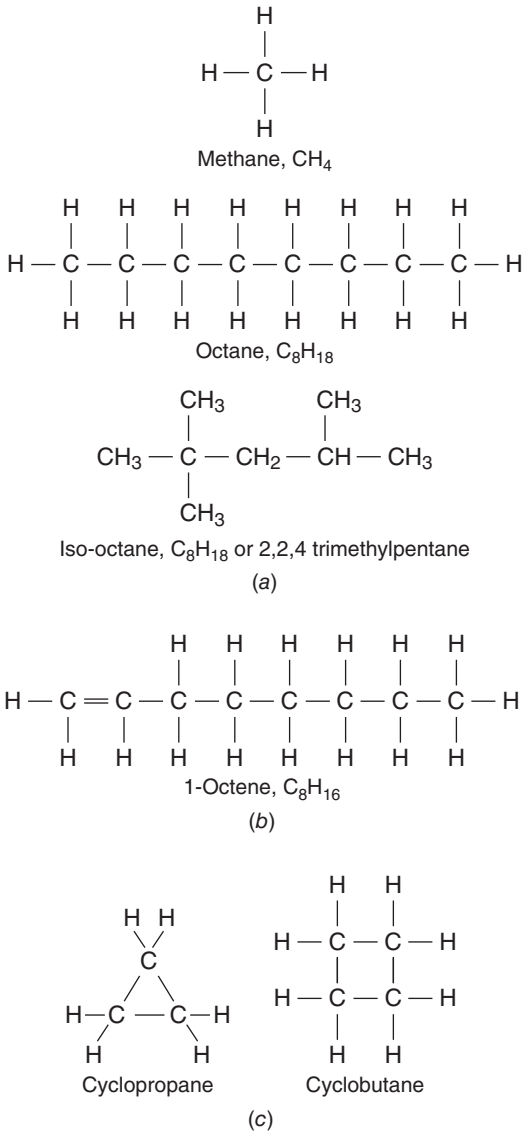


Figure 1.2 (*a*) Paraffins, (*b*) olefins, and (*c*) naphthenes.

Iso-octane, shown in Figure 1.2, is an example of a highly branched chain isomer of octane. That is, it has the same number of carbon atoms as octane but not in a straight chain. The group CH_3 attached to the second and fourth carbons from the right is called a methyl radical, *meth* because it has one carbon atom, *yl* because it is of the alkyl radical family $C_nH_{(2n+1)}$, and *radical* because it is a molecule that contains at least one unpaired valence electron, which makes it very reactive. Iso-octane is more properly called 2,2,4-trimethyl pentane, 2, 2, 4 because methyl groups are attached to the second and fourth carbon atoms, *trimethyl* because three methyl radicals are attached, and *pentane* because the straight chain has five carbon atoms.

Olefins (alkenes) are molecules with one or more carbon=carbon double bonds. Mono-olefins have one double bond, the general formula C_nH_{2n}, and their names end with *-ene*. The molecule 1-octene, C_8H_{16} is shown in Figure 1.2. Isomers are possible not only by branching the chain with

the addition of a methyl radical but also by shifting the position of the double bond without changing the carbon skeleton. Olefins with more than one carbon=carbon double bond are undesirable components of fuel that lead to storage problems. Consequently, they are refined out and the only olefins of significance in diesel fuel or gasoline fuel are mono-olefins.

Naphthenes (cycloalkanes) have the same general formula as olefins, C_nH_{2n}, but there are no double bonds. They are called *cyclo* because the carbon atoms are in a ring structure. Two examples are cyclopropane and cyclobutane, shown in Figure 1.2. Cycloalkane rings having more than six carbon atoms are not as common.

Aromatics are hydrocarbons with carbon=carbon double bonds internal to a ring structure. The most common aromatic is benzene, shown schematically in Figure 1.3. Benzene is a regulated toxic compound, as it is a known carcinogen. Notice that the double bonds alternate in position between the carbon atoms. This makes the molecule's bonds difficult to break, so that a greater temperature is required to initiate combustion. As a result, aromatics are desirable in gasoline since they increase the octane number. Aromatics are undesirable components of diesel fuels. Some common aromatics (toluene, ethylbenzene, and styrene) have groups such as methyl radicals substituted for hydrogen atoms, and others (biphenyl) have more than one ring. Finally, there are polycyclic aromatic hydrocarbons (PAHs) which are aromatics with two carbon atoms shared between more than one ring (naphthalene and anthracene).

An alcohol is a partially oxidized hydrocarbon, formed by replacing a hydrogen atom with the hydroxyl radical OH. If the hydrogen atom attached to an aromatic ring is replaced by the hydroxyl radical, the molecule is called a phenol. Ethers are isomers of alcohol with the same number of carbon atoms. Some examples, shown in Figure 1.4, are methanol, ethanol, phenol, and methyl ether.

Nitromethane CH_3NO_2 is formed from a paraffinic hydrocarbon by replacing a hydrogen atom with a NO_2 group, as shown in Figure 1.4. It has twice the bound oxygen as monohydric alcohols

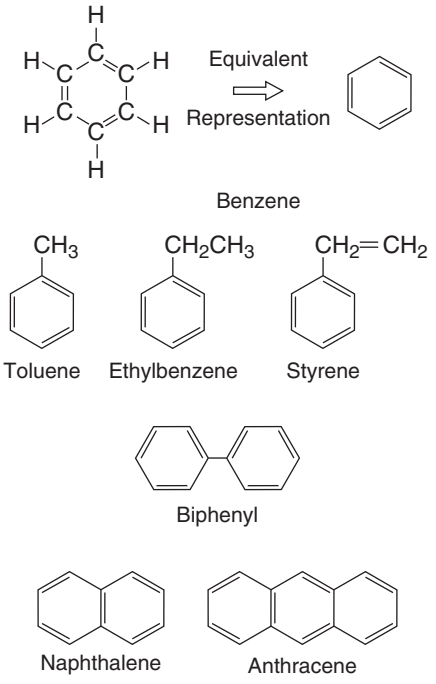


Figure 1.3 Aromatics.

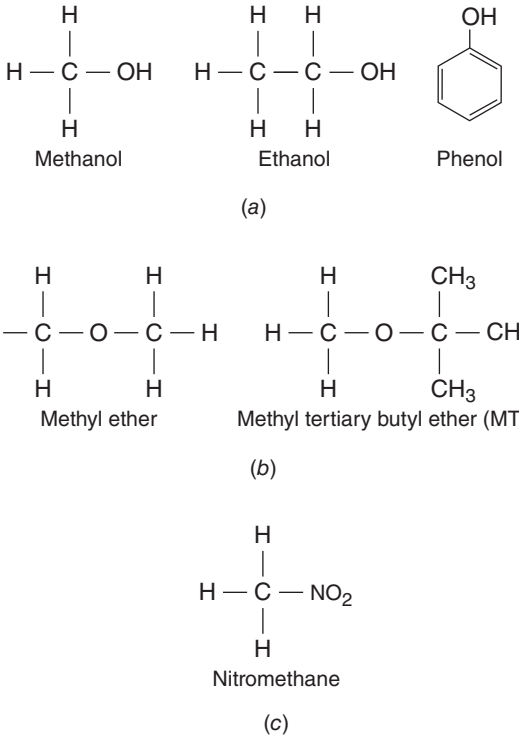


Figure 1.4 (*a*) Alcohols, (*b*) ethers, and (*c*) nitroparaffins.

and can combust without air. At ambient temperature, it is a liquid, and it is widely used as a drag racing fuel.

Crude oil is physically separated into various fractions, and then chemically processed into fuels and other products in an oil refinery. A full-scale crude oil refinery produces fuels for engines (gasoline, diesel, and jet), fuels for heating (burner, coke, kerosene, and residual), chemical feedstock (aromatics and propylene), and asphalt. On the average, a refinery will refine about 40% of the input crude oil into gasoline, 20% into diesel and heating fuel, 15% into residual fuel oil, 5% into jet fuel, and the remainder into the other listed hydrocarbons. The fraction separation process is called distillation and the device employed is a fractionating column.

Alkylation is used to increase the molecular mass and octane number of gasoline by adding alkyl radicals to a gaseous hydrocarbon molecule. Light olefin gases are reacted with iso-butane using a catalyst. Iso-octane results from reacting butene with iso-butane. This process requires relatively low temperature (275 K) and pressure (300 kPa) and, therefore, consumes relatively less energy than other refining processes.

Catalytic cracking uses activated catalysts to break the molecular chains of a distillate to produce naphthas. Naphtha is a liquid mixture consisting of straight-chained and cyclic aliphatic hydrocarbons having from five to nine carbon atoms per molecule. The naphtha products of catalytic cracking are blended with other hydrocarbons to produce high octane number gasolines. The reactions are at high temperature (700–800 K) and at low to moderate pressure (200–800 kPa). Considerable energy is consumed in the process.

Reforming refers to reactions designed to alter the molecular structure to yield higher octane gasoline (e.g., conversion of paraffins into aromatic hydrocarbons). This is often done using catalysts in a hydrogen atmosphere at high temperature (800 K) and high pressure (3000 kPa).

Considerable hydrogen is produced as a result of the reaction:

$$C_nH_{2n+2} \longrightarrow C_nH_{2n-6} + 4H_2$$

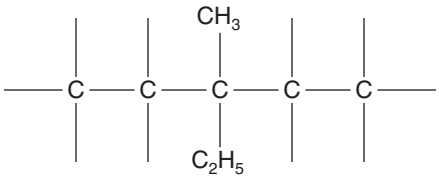
Coking is the process used to convert heavy reduced crude fractions to the more usable naphtha and distillate fractions. Upon heating, the molecules undergo pyrolytic decomposition and recombination. The average molecular mass of the fraction remains the same, but a greater spectrum of components is produced. The heaviest component, called coke, is a solid carbon material similar to charcoal.

Example 1.1 ***Fuel Chemical Structure***

What is the chemical structure of (a) 3-methyl-3-ethylpentane?

Solution

This pentane has methyl CH_3 and an ethyl C_2H_5 on the third carbon. A pentane paraffin has five single-bonded carbon atoms. Its chemical formula is C_8H_{18}, so it is an isomer of octane. Its structure is:



1.7 Gaseous and Liquid Fuels for Combustion Engines

In this section, we introduce the gaseous and liquid fuels used in combustion devices such as internal combustion engines, gas turbines, and thermal power generation. Spark ignition engine fuels include natural gas, propane, hydrogen, gasoline, ammonia, methanol, and ethanol.

Table 1.1 compares the thermal properties of a variety of gaseous fuels. The lower heat of combustion q_{lhc} or heating value is defined as the state where all of the water in the products is vapor (the quality $\chi = 1$), and the higher heat of combustion, q_{hhc}, or heating value is defined

Table 1.1 Thermodynamic Properties of Common Gaseous Fuels.

Fuel	Hydrogen H_2	Methane CH_4	Ammonia NH_3	Propane C_3H_8
Boiling Temperature (°C) at 1 atm	−253	−161	−33.4	−42.1
Condensation Pressure (atm) at 25 °C	n/a	n/a	9.90	9.40
Lower Heat of Combustion q_{lhc} (MJ/kg)	120	50	18.6	46.4
Flammability Limits ϕ (Lean–Rich Equivalence Ratios)	0.10–7.1	0.50–1.7	0.63–1.40	0.51–2.5
Adiabatic Flame Temperature $T_{f,ad}$ (K)	2383	2240	1800	2268
Maximum Laminar Flame Speed S_L (m/s)	2.91	0.37	0.07	0.43
Minimum Autoignition Temperature (°C)	520	630	650	450

as the state where all of the water in the products is liquid (the quality $\chi = 0$). At $T = 298\,\text{K}$, the enthalpy of vaporization of water $h_{\text{fg}} = 2442\,\text{kJ/kg}$ on a mass basis, and $\overline{h}_{\text{fg}} = 43.99\,\text{kJ/mol}$ on a molar basis. Thermal properties of fuels and associated measurements are discussed further in Chapter 2, and tables of transport properties of fuels are provided in the Appendix E.

In the United States, petroleum gasoline is currently the dominant fuel for internal combustion engines, as it comprises about 70% of the vehicular fuel consumption, followed by diesel fuel at 23%, ethanol at 5%, and biodiesel at 0.5%. The performance of spark ignition engines is limited by the occurrence of an autoignition process called knock, which constrains the maximum compression ratio and thus the overall engine efficiency. Compression ignition engines have separate fuel and air streams that combust as they are mixed together at a temperature greater than the autoignition temperature, a process called diffusion combustion. The performance of compression ignition engines is limited by emissions of unburned hydrocarbons such as soot.

Example 1.2 ***Hydrogen Heat of Combustion***

If the mass lower heat of combustion q_{lhc} of hydrogen H_2 is 120 MJ/kg, what is its molar high heat of combustion $\overline{q}_{\text{hhc}}$?

Solution

The hydrogen combustion reaction is

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

where 1 mol of hydrogen yields 1 mol of water. Converting q_{lhc} to a molar basis, where M_{H_2} is the molar mass (kg/kmol) of hydrogen,

$$\begin{aligned}\overline{q}_{\text{hhc}} &= q_{\text{lhc}} M_{H_2} + n_{H_2O}\overline{h}_{\text{fg}} \\ &= (120)(2.016) + (1)(43.99) \\ &= 286\,\text{MJ/kmol}\end{aligned}$$

1.7.1 Methane and Natural Gas

Natural gas is a naturally occurring gaseous fuel found in oil fields. It is primarily composed of about 90–95% methane (CH_4), with small amounts of additional compounds such as 0–4% nitrogen, 4% ethane, and 1–2% propane. Due to its structure, methane is a greenhouse gas and, over a 20-year period, has a global warming potential about 80 times that of carbon dioxide.

Since methane has a lower carbon to hydrogen ratio relative to gasoline, the CO_2 emissions from the combustion of methane are about 22–25% lower when compared to gasoline combustion. Natural gas has been used for many years for electric power generation, industrial processes, and commercial and residential heating. An extensive distribution network of natural gas pipelines exists to meet the need for natural gas for applications.

Natural gas has slow ignition kinetics and a low cetane number. The combustion of methane is different from that of higher order hydrocarbon combustion since only carbon–hydrogen bonds are involved, and no carbon=carbon bonds, so the combustion process is more likely to be more complete, producing less non-methane hydrocarbons. Optimal thermal efficiency occurs at rich conditions with equivalence ratios from 1.3 to 1.5. The combustion reactions of methane produce intermediate molecules, such as formaldehyde, a criteria pollutant. Since it is spark ignited, the particulate emissions of methane are very low relative to diesel fuel. Methane has a lower adiabatic

flame temperature (2240 K) than that of gasoline (2310 K), due to its greater product water content. Operation under lean conditions will also lower the peak combustion temperature.

Natural gas is stored in a compressed (CNG) state at room temperature and also in a liquid (LNG) form at −160 °C. Natural gas is pressurized to 20 MPa in vehicular storage tanks and has about one-third of the volumetric energy density of gasoline. The storage pressure is about 20 times that of propane.

Natural gas-fueled vehicles have been in use since the 1950s, and conversion kits are available for both spark and compression ignition natural gas and gasoline or diesel fuel. Like propane, natural gas is delivered to an internal combustion engine through a pressure regulator, either through a mixing valve located in the intake manifold, port fuel injection at about 750 kPa, or through direct injection into the cylinder. With intake manifold mixing or port fuel injection, the engine's volumetric efficiency and power are reduced due to the displacement of about 10% of the intake air by the natural gas, and the loss of evaporative charge cooling. Natural gas does not require mixture enrichment for cold starting, reducing potential cold start HC and CO emissions. Natural gas has an octane number (RON) of about 120, so that natural gas-fueled engines can operate at a compression ratio greater than that of gasoline fueled engines.

1.7.2 Propane

Propane (C_3H_8) is a saturated alkane hydrocarbon. When blended with butane C_4H_{10} or ethane C_2H_6, it is also designated as liquefied petroleum gas (LPG). A common LPG blend is P92, which is 92% propane and 8% butane. Propane is a by-product of crude oil refining and natural gas processing. In the United States, about one-half of the LPG supply is obtained from the lighter hydrocarbon fractions produced during crude oil refining, and the other half from heavier components of wellhead natural gas.

Propane has been used as a vehicular fuel since the 1930s. As of 2020, there are about 10 million LPG vehicles operating worldwide. There is a relatively extensive refueling network for propane. For example, there are about 15,000 refueling stations available in North America. There are a number of original equipment manufacturers that currently sell propane-fueled vehicles, primarily light- and medium-duty fleet vehicles, such as pickup trucks and vans.

In vehicles, propane is stored as a compressed liquid, at about 1 MPa (10 atm) pressure. Its evaporative emissions are essentially zero, since it is used in a sealed system. A pressure regulator controls the supply of propane to the engine and converts the liquid propane to a gas through a throttling process. As the pressure is reduced in the pressure regulator, the propane vaporizes into a gas. Propane gas can be injected into the intake manifold, into the ports, or directly into the cylinder. Propane has an octane number of 112 RON, so vehicular applications of propane can operate at a raised compression ratio.

1.7.3 Hydrogen

Hydrogen (H_2) can be produced from many different feedstocks, including natural gas, coal, biomass, and water. The production processes include steam reforming of natural gas, presently the most economical method, gasification of coal, and electrolysis of water. The various methods used to produce hydrogen as a fuel are classified by color. "Green" hydrogen is produced using renewable energy (wind and solar) to split H_2O into H_2 and O_2, which generates no greenhouse gases. Currently, most hydrogen is produced from natural gas and is denoted "gray" hydrogen. "Blue" hydrogen also uses natural gas with the added step of capturing and storing the

carbon-dioxide emissions. The steam reforming process using natural gas to produce "gray" or "blue" hydrogen is given in Eq. (1.1):

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2 \tag{1.1}$$

Hydrogen is a colorless, odorless, and nontoxic gas, and hydrogen flames are invisible and smokeless. The global warming potential of hydrogen is insignificant in comparison to hydrocarbon-based fuels since the combustion of hydrogen produces no carbon-based compounds such as HC, CO, and CO_2. At present, the largest user of hydrogen fuel is the aerospace community for rocket fuel.

The combustion characteristics of hydrogen are very different from gasoline, as the laminar flame speed of a hydrogen–air mixture is about 3 m/s, about 10 times that of methane and gasoline, and the adiabatic flame temperature is about 100 °C higher than gasoline and methane. Since it has wide flammability limits (5–75% by volume), preignition and backfiring in an internal combustion engine can be a problem. The flammability limits correspond to equivalence ratios of 0.10–7.1. Water injection into the intake manifold of an engine is used to mitigate preignition and provide cooling. The relatively high octane rating of hydrogen of 106 RON allows the use of an increased compression ratio.

There have been a number of hydrogen vehicular demonstration projects, but the relatively high cost of hydrogen fuel has hindered adoption as an alternative fuel. Hydrogen produced by onboard electrolysis of water can also be injected into the intake manifold of diesel engines to reduce soot emissions.

One of the major obstacles related to the use of hydrogen fuel is the lack of a manufacturing, distribution, and storage infrastructure. The most economical method would be to distribute hydrogen through pipelines, similar to natural gas distribution. It has been proposed to blend relatively low (5–15%) concentrations of hydrogen with natural gas and use the natural gas distribution infrastructure for distribution of the hydrogen-natural gas blend. This concept is not new, since coal gas, a blend of hydrogen and methane, was used in gas distribution systems in the 1800s until replaced by natural gas.

The three methods used to store hydrogen are: (1) in a liquid form at −253 °C in cryogenic containers; (2) as a metal hydride, such as iron–titanium hydride FeTi H_2, or (3) in a pressurized gaseous form at 20–70 MPa. The metal hydride releases hydrogen when heated by a heat source, such as a vehicle exhaust system. The most common storage methods are liquid and hydride storage, which have comparable volumetric storage capabilities, both requiring about 10 times the space required by an equivalent 5-gallon gasoline tank.

Compressed hydrogen at 70 MPa has one-third the energy density by volume of compressed natural gas, and liquid hydrogen has one-fourth the energy density by volume of gasoline. The use of liquid hydrogen has an additional energy cost, as liquefaction of hydrogen to a temperature of 20 K requires an expenditure of energy approximately equal to the energy content of the liquid hydrogen. If mixed with air in the intake manifold of an engine, the volume of hydrogen is about 30% of the intake mixture volume at stoichiometric, decreasing the volumetric efficiency. The techniques used to reduce NO_x levels in hydrogen combustion are retarding the spark ignition timing, exhaust gas recirculation, and leaner operation to offset the effect of higher flame speeds and combustion temperatures.

1.7.4 Ammonia

Ammonia (NH_3) is a carbon-free fuel formed using the Haber–Bosch process, a catalytic synthesis reaction of hydrogen and nitrogen, invented in 1913. Since the combustion of ammonia produces

no carbon-based compounds, ammonia has the potential to contribute to the decarbonization of engine fuels. The production and transport technologies of ammonia are mature. Ammonia has been mainly used for the past hundred years as a chemical raw material, for the production of fertilizer, and as a working fluid in refrigeration cycles. It is also used as a reducing agent in selective catalytic reduction (SCR) of NO_x in thermal power generation and in internal combustion engines.

Ammonia is a fuel that can be obtained from fossil fuels, biomass, or other renewable sources. Some advantages of ammonia with respect to hydrogen are its lower cost per unit of stored energy, higher volumetric energy density, easier production, handling and distribution, and better commercial viability. Ammonia has a narrow flammability range and is therefore generally considered nonflammable when transported.

Ammonia concentrations in air are regulated due to its high level of toxicity. The OSHA 8 hour NH_3 exposure limit is 25 ppm, and the immediately dangerous to life and health (IDLH) limit is 300 ppm.

The thermal properties of ammonia, such as condensation pressure and boiling temperature, are very similar to that of propane. At 25 °C, it can be stored as a liquid at pressures greater than 10 bar, with a density of 603 kg/m^3. The lower heat of combustion $q_{\mathrm{lhc}} = 18.6$ MJ/kg of ammonia is 40% of the heat of combustion of propane. The stoichiometric laminar flame speed at atmospheric pressure is 7.0 cm/s, a factor of about five slower than that of hydrocarbon fuels. The slow flame speed results in poor combustion quality in engines, so combustion promoters such as hydrogen, kerosene, gasoline, or diesel fuels are required. The adiabatic flame temperature of ammonia is 1800 K, lower than that of hydrocarbon fuels, and the autoignition temperature is relatively high at about 650 K.

1.7.5 Gasoline

Gasoline is a hydrocarbon fuel composed of a blend of light distillate hydrocarbons, including paraffins, olefins, naphthenes, and aromatics. It has a hydrogen to carbon ratio varying from 1.6 to 2.4. A typical formula used to characterize gasoline is C_8H_{15}, with a molecular mass of $M = 111$. A high hydrogen content gasoline is C_7H_{17}. Gasoline properties of interest for internal combustion engines include the octane number, volatility, gum content, viscosity, specific gravity, and sulfur content. The American Society for Testing and Materials (ASTM) has established a set of gasoline specifications for each property.

Gasoline has been the major vehicular liquid fuel for spark ignition engines since the early 1900s. It has a very high volumetric energy density, a relatively low cost, and reliable cold-weather startup properties. It has the highest fueling station accessibility of engine fuels. Gasoline-fueled engines are also adaptable to alternative fuels such as propane and natural gas.

1.7.6 Methanol

Methanol (CH_3OH) is an alcohol fuel formed from natural gas, coal, or biomass feedstock. Methanol has been used as a vehicular fuel since the early 1900s and is also used as a fuel for diesel engines and fuel cells. It is also called wood alcohol. It is a liquid at ambient conditions. Its chemical structure is a hydrocarbon molecule with a single hydroxyl (OH) radical. The hydroxyl radical increases the polarity of the hydrocarbon, so that methanol is miscible in water and has a relatively low vapor pressure. Since oxygen is part of the chemical structure, less air is required for complete combustion. Methanol is very toxic, and ingestion can cause blindness and death.

To form methanol, the feedstock, such as natural gas, is steam reformed to make CO and H_2,

$$CH_4 + H_2O \longrightarrow CO + H_2 \tag{1.2}$$

Methanol is then synthesized by the subsequent reaction of CO and H_2,

$$CO + 2H_2 \longrightarrow CH_3OH \tag{1.3}$$

Pure methanol is labeled M100, and a mix of 85% methanol and 15% gasoline is labeled M85, with an octane rating of 102. The octane rating of methanol M100 of 111 RON allows the use of an increased compression ratio. Methanol is partially miscible with gasoline. The low volatility of methanol requires priming agents such as gasoline for improving cold starting performance. Adding gasoline to methanol provides more volatile components that can vaporize more easily at low temperatures. Satisfactory cold starting with M85 requires a rich mixture so that enough volatiles are present to form a combustible mixture.

Methanol has been adopted as a racing fuel, both for performance and for safety reasons. Since methanol is highly miscible with water, a methanol fire can be extinguished with water, which is not the case with gasoline. The relatively high enthalpy of evaporation (1215 kJ/kg) of methanol relative to gasoline (310 kJ/kg) produces greater intake aircooling and a corresponding increase in volumetric efficiency relative to gasoline. The energy density by volume of methanol is about half that of gasoline. However, because of its oxygen content, it has a higher stoichiometric energy density (3.09 MJ/kg_{air}) relative to gasoline (2.96 MJ/kg_{air}). For maximum power, a rich equivalence ratio of $\phi = 1.6$ is used.

1.7.7 Ethanol

Ethanol (C_2H_5OH) is an alcohol fuel formed from the fermentation of sugar and grain stocks, primarily corn and sugar cane, which are renewable energy sources. Its properties and combustion characteristics are very similar to those of methanol. Ethanol is also called "grain" alcohol. It is a liquid at ambient conditions and nontoxic at low concentrations.

Gasohol (E10) is a gasoline–ethanol blend with about 10% ethanol by volume. E85 is a blend of 85% of ethanol and 15% of gasoline. In the United States, the primary source of ethanol is currently from starch feedstocks, such as corn. As a result of the 2005 Renewable Fuel Standard which mandates that gasoline contain 10% biofuels, in 2016, about 40% of the U.S. corn production was used to produce ethanol. In Brazil, about half of the vehicles use an ethanol-based fuel "alcool," primarily E93, produced from sugar cane. There are efforts underway to produce ethanol from cellulosic feedstocks such as corn fiber, forestry waste, and switch grass.

The energy density by volume of ethanol is relatively high for an alternative fuel, about two-thirds that of gasoline. The octane rating of ethanol of 111 RON allows the use of an increased compression ratio. The cetane number of ethanol is low, at about 8, and it can be used in compression ignition engines with diesel fuel pilot ignition.

1.7.8 Kerosene

Kerosene is a liquid fuel composed of a mixture of hydrocarbon molecules with a range of 9–16 carbon atoms per molecule. The major components are branched and straight-line alkanes and naphthenes. Kerosene is often approximated by dodecane ($C_{12}H_{26}$). It is produced by the fractional distillation of petroleum and condenses at a temperature between diesel fuel and gasoline. Accordingly, at standard conditions, its volatility, i.e., vapor pressure of 0.7 kPa, is between a diesel fuel

vapor pressure of 0.007 kPa and a gasoline vapor pressure of 60 kPa. Kerosene is mainly used as an aviation gas turbine fuel (Jet A) and as a rocket fuel (RP-1). Other uses include home heating and cooking.

1.7.9 Octane Number

To provide a standard measure of a spark ignition fuel's knock characteristics, a scale has been devised in which fuels are assigned an octane number, *ON*. A knock scale was developed in the 1920s by the American Society for Testing Materials (ASTM) Cooperative Fuel Research Committee (CFR). There are two fuels used, one with a low resistance to knock and the other with a high resistance to knock. In the ASTM octane scale, the low primary reference fuel is straight-chain *n*-heptane, assigned an octane number of 0, with a very short ignition delay. The high primary reference fuel is branched chain iso-octane, assigned an octane number of 100, with a much longer ignition delay. These two fuels were chosen as they also have very similar thermodynamic properties, with densities of 0.68 kg/m^3, boiling points of 99 °C, and vapor pressures of 5.3 kPa at 25 °C.

The ASTM CFR Committee worked with the Waukesha Motor Company to develop a standardized CFR fuel research engine and specific operating conditions to measure the octane number of a fuel. The first CFR engine was designed and built in 1929 and is still the standard by which liquid fuel octane measurements are made today. An antiknock index (AKI) is the average of the research (ASTM D2699) and motored (ASTM D2700) octane numbers and is displayed on gasoline pumps at service stations (e.g., 85, 87, and 91). In general, it has been found that the octane number is increased by reducing the straight-chain length of the hydrocarbon fuel. This can be accomplished by reducing the total number of carbon atoms or by rearranging them into a branch chain structure.

Many compounds have been tested for use as octane improvers in gasoline. Tetraethyl lead was the primary octane improver in general use from 1923 to 1975. Its use in motor vehicles was prohibited in 1995 due to its toxicity and its adverse effect on catalytic converters and oxygen sensors. Currently, lead is only used in aviation and off-road racing gasolines. Thomas Midgley (1889–1944), a mechanical engineer from the General Motors Research Laboratory, discovered lead additives in 1921. Lead deactivates the free radicals produced during the combustion process, thus decreasing the rate of heat release. As an aside, Midgley also was the inventor of Freon (F-12), a refrigerant initially developed for automotive air conditioning systems. Freon was the most widely used refrigerant in the world until the mid-1990s when it was determined that the ultraviolet decomposition of Freon in the stratosphere releases chlorine, causing depletion of the stratospheric ozone layer. The manufacturing of Freon in the United States was prohibited in 1998.

1.7.10 Methane Number

The methane number *MN* is a measure of the tendency for a gaseous fuel to knock. A fuel's methane number limits the maximum compression ratio and thus the theoretical engine efficiency. A blend of 20% hydrogen and 80% methane has $MN = 80$. As indicated in Table 1.2, Malenshek and Olsen (2009) found a linear relationship between the maximum compression ratio and the methane number, for a variety of gaseous fuels, including coal gas, wood gas, digester gas, and landfill gas. An engine optimized to operate on natural gas with a methane number of about 90 is susceptible to knock when operated on gases that have a lower methane number, such as coal gas which has a methane number of 24. The octane number of methane is 120 RON, one of the highest values for hydrocarbon fuels.

Table 1.2 Critical Compression Ratio versus Methane Number.

Gas	Compression Ratio	Methane Number
Coal Gas	8.0	23.9
Steam Reformed Natural Gas	10.5	62.4
Wood Gas	10.3	70.2
Natural Gas		78–98
Methane	14.4	100
Digester Gas	17.6	139.1
Landfill Gas	17.6	139.6

Source: Adapted from Malenshek and Olsen (2009).

Example 1.3 ***Fuel Mixtures***

A flexible fuel engine operates with a mixture of 35% gasoline and 65% methanol, by volume. If the combustion is to be stoichiometric, what should the mass air–fuel ratio be?

Solution

The volume or mole fraction $X_i = V_i/V$, and the mass fraction $Y_i = m_i/m$ are reviewed in Section 2.2, and stoichiometry is reviewed in Section 2.10. The volume fractions X_i are to be converted to mass fractions. Writing the mass fraction Y_i in terms of density ρ_i and X_i.

$$Y_i = \frac{m_i}{m} = \frac{\rho_i \cdot V_i}{\sum \rho_i \cdot V_i} = \frac{\rho_i \cdot V_i/V}{\sum \rho_i \cdot V_i/V} = \frac{\rho_i \cdot X_i}{\sum \rho_i \cdot X_i}$$

Using data from Table 1.3,

Fuel	Formula	X_i	ρ_i	$\rho_i X_i$	Y_i	$AF_{st,i}$
Gasoline	C_8H_{18}	0.35	710	248.5	0.324	15.04
Methanol	CH_3 OH	0.65	796	517.4	0.675	6.43
Sum		1.0		765.9		1

The mass air–fuel ratio is the weighted sum of the stoichiometric air–fuel ratios of the two fuels.

$$\begin{aligned} \mathrm{AF_{st}} &= \sum \mathrm{AF_{st,}}_i \cdot x_i \\ &= 15.04 \cdot 0.324 + 6.43 \cdot 0.675 \\ &= 9.22 \end{aligned}$$

1.7.11 Diesel Fuels

Diesel fuel for compression ignition engines consists of a mixture of light distillate hydrocarbons that have molecular masses from about 170 to 200 kg/kmol with a corresponding range of 12–20 carbon atoms per molecule. Diesel fuels vaporize in the range between about 180 and 360 °C, higher than gasoline. It is estimated that there are more than 10,000 isomers in diesel fuel. Like gasoline, diesel fuels are mixtures of paraffinic, olefinic, naphthenic, and aromatic hydrocarbons, but

Table 1.3 Thermodynamic Properties of Spark Ignition Liquid Fuels.

	Gasoline	Ethanol	Methanol	Kerosene
Molecular Mass, M (kg/kmol)	~110	46.07	32.04	~170
Stoichiometric Air–Fuel Ratio, AF_s	15.04	8.94	6.43	14.92
Lower Heat of Combustion, q_{lhc} (MJ/kg)	44.5	26.8	19.9	43.1
Liquid Density, ρ_l (kg/m^3) at 15 °C	710	794	796	800
Enthalpy of Vaporization, h_{fg} (kJ/kg) at 298 K	310	850	1215	251
Adiabatic Flame Temperature (K)	2310	2197	2151	2094
Autoignition Temperature (°C)	280–370	365	470	220
Flammability Limits (% Volume)	1.4–7.6	3.5–26	5.5–26	0.6–4.9
Research Octane Number (RON)	90–98	111	112	20-50
Motor Octane Number (MON)	80–90	92	91	20-50
Vapor Pressure (kPa) at 32 °C	62–90	17	32	0.7
Boiling Point T_{sat} (°C) at 1 bar	30–225	−42	−160	200–260

Source: Adapted from Owen and Coley (1995).

their relative proportions are different. In CFD simulations, diesel fuel is often approximated by tetradecane (n-$C_{14}H_{30}$) for computation of spray breakup, evaporation, and mixing. The ignition and combustion characteristics of diesel fuel are approximated by n-heptane (n-C_7H_{16}), as its cetane number of 56 is approximately equal to that of Diesel 2-D.

Diesel fuels have about an 8% greater energy density by volume than gasoline and are the primary fuel used by heavy duty vehicles. Diesel fuel is also much less flammable than gasoline, as the flashpoint temperature of diesel 2-D is 52 °C, much higher than that of gasoline, which is about −40 °C. The flash point is defined as the lowest temperature at which a vapor–air mixture will ignite when an ignition source is applied, in contrast to the autoignition temperature, which has no ignition source.

Diesel fuels are named after Rudolph Diesel (1858–1913) who in 1897 was the first to develop an engine designed for compression ignition. In a compression ignition engine, a low volatility fuel must be converted from a liquid state into a finely atomized state, vaporized, mixed with air, and its temperature raised to a point to support autoignition. The autoignition temperature of vehicular diesel fuel (2-D) is about 530 K, about 110 K less than that of gasoline.

Diesel fuels are classified by cetane number (*CN*) and compared using an ignition delay metric. The cetane number characterizes the ability of the fuel to autoignite and is the opposite of the octane number. The range of cetane numbers *CN* for vehicular diesel fuels is from about 40–60. As the cetane number is increased, the ignitability of the fuel increases, with a decrease in the ignition delay time. If the cetane number is low, the ignition delay is long, and fuel will not ignite until late in the injection process. In this situation, the fuel is well mixed, so that once combustion is initiated, the burning rate is controlled by the chemical kinetics.

Aromatic hydrocarbons and alcohols have strong chemical bonds, resulting in a long ignition delay. If these fuels mix completely with air before autoignition occurs, when ignition does occur, they will all burn rapidly in a premixed phase, producing a large rate of change of pressure and a high peak pressure. If the cetane number is too low, the engine will misfire and exhibit poor cold start behavior.

At higher cetane numbers, with shorter ignition delays, combustion is initiated while the fuel is being injected. The chemical bonds of some fuels, such as alkanes (straight-chain paraffins), are easily broken. Relatively little fuel burns in the premixed phase and most of the fuel burns in a diffusion phase at a rate limited by the rate of mixing with the cylinder air. If the cetane number is too high, combustion can occur before the fuel and air are completely mixed, resulting in increased soot formation.

One component of diesel fuel that has attracted particular regulatory attention is sulfur, due to the adverse impact that sulfur-containing particulate emissions have on air quality. During combustion, the sulfur in the diesel fuel forms sulfates (SO_4^-), and sulfur dioxide (SO_2), which reacts with water to form sulfuric acid, a component of acid rain. Ultralow sulfur diesel (ULSD) has a sulfur content of 15 ppm or less. As part of the Euro V emission standards, ULSD is required in Europe. After December 1, 2014, all highway, non-road, locomotive and marine diesel fuel produced and imported in the United States was mandated to be ultralow sulfur.

1.7.12 Alternative Compression Ignition Fuels

A variety of fuels have been developed as an alternative for petroleum-based diesel fuels. Alternative diesel fuels have a higher cost, and lower volumetric energy density than fossil-based diesel fuel, but do produce lower CO and particulate emissions. Biodiesel fuels are manufactured from their corresponding vegetable oils, through the trans-esterification process, where one ester is converted into another. Biodiesel is produced from vegetables such as soybean, castor, canola, sunflower, cotton, palm, coconut, jatropha, and algae. Interest in algae-based biodiesel has been increasing, due to the far greater sunlight–oil conversion efficiency of algae relative to land-based crops; however, the production costs remain relatively noncompetitive.

Biodiesel fuels are produced through the trans-esterification of the triglycerides in vegetable oil using a low molecular mass alcohol, such as methanol. The esterification process decreases the kinematic viscosity of the neat vegetable oil from about 30×10^{-6} to about 4×10^{-6} m^2/s, for satisfactory operation of the fuel injectors. Typical chemical syntheses of biodiesel fuels depend on the distribution of the triglycerides in their corresponding vegetable oils.

Trans-esterification is basically a substitution of methanol (a monohydric alcohol) for the triglycerides. The methyl ester is obtained through a process in which methyl alcohol and a catalyst (such as sodium hydroxide or potassium hydroxide) chemically breaks down the triglyceride molecule into a fatty acid methyl ester (FAME) of the oil and a glycerin byproduct. Due to chemical equilibrium considerations, not all of the tri-, di-, and mono-glycerides can be removed in the esterification process.

Biodiesel is not a single chemical compound, as the triglycerides in vegetable oils are a variable mixture of unsaturated and saturated fatty acids. As shown in Table 1.4, a representative biodiesel formula is $C_{19}H_{35}O_2$. The iodine number is used as a measure of the degree of unsaturated bonds in biodiesel fuel, with higher iodine numbers indicating more unsaturated carbon=carbon double bonds in the fuel molecule. The test method used to determine the iodine number is ASTM D1959.

Biodiesels are fully miscible with conventional diesel fuel and can be blended at various levels denoted by the volume percent of biodiesel. Biodiesel fuels are designated with the prefix B, so a mixture of 20% biodiesel is labeled B20. Diesel engines are rated for a maximum percentage of biodiesel, typically from B5 to B20. The most common blend in the United States is B20. In Europe, diesel fuel is blended with 7% biodiesel to produce B7. If 5% ethanol is added to B20, the resulting blend is labeled B20E5.

Table 1.4 Comparison of Thermodynamic Properties of Various Compression Ignition Fuels.

	Diesel (2D–4D)	Dimethyl Ether (DME)	Bio-diesel (B100)
Chemical Formula	$C_{15}H_{25}$	$CH_3\ OC\ H_3$	$C_{19}H_{35}O_2$
Molecular Mass (kg/kmol)	170–200	46.07	295
Cetane Number	40–60	55–60	48–58
Liquid Density (kg/m^3)	775–860	668	882
Autoignition Temperature (°C)	256	350	375–450
Stoichiometric A/F Ratio	14.5–14.4	9.0	11.2–12.5
Kinematic Viscosity (m^2/s) at 40 °C	2.8×10^{-6}	2.2×10^{-7}	4.1×10^{-6}
Lower Heating Value[a], Mass (MJ/kg$_{fuel}$)	43.2–42.8	28.4	37.7
Lower Heating Value[a], Volume (MJ/l$_{fuel}$)	33.7–36.8	19.0	33.25
Thermal Expansion Coefficient (%/K)	8.4×10^{-4}		
Boiling Point at 1 bar (°C)	180–360	−25	328–366
Vapor Pressure at 38 °C (bar)	0.0069	8	1×10^{-8}

a) Equivalent to the lower heat of combustion.

In cold climates, it can be a challenge to fuel vehicles with high blends of biodiesel because the biodiesel cloud points and pour points occur at higher temperatures relative to conventional diesel. The cloud point of soybean biodiesel is about 1 °C, whereas the cloud point for No. 1 diesel is about −40 °C. The difference between the cloud point and the pour point for soybean biodiesel is about 1 °C, whereas the difference for No. 1 diesel is about 20 °C.

Two additional compression ignition fuels with high cetane numbers are dimethyl ether (DME) and Fischer–Tropsch (F–T) fuel. DME, CH_3OCH_3 (see Table 1.4), is an oxygenated fuel produced by dehydration of methanol, from lignocellulosic biomass, or from synthesis gas. It has a relatively low autoignition temperature and a short ignition delay, as indicated by its cetane number $CN = 55$–60. DME is composed of two methyl groups linked by an oxygen atom and has the same atomic composition as ethanol, with a greater adiabatic flame temperature. It burns with a visible blue flame, similar to that of natural gas. It has low lubricity, so its use in engines requires lubricity additives, such as a fatty acid lubricity improver. Since its vapor pressure is between propane and butane, it is a gas at standard conditions. In vehicles, a fuel tank pressurized to about 5 bar, similar to pressures used for LPG storage, is required to store DME in liquid form. It is noncorrosive to metals but does deteriorate some elastomers. The volumetric energy density (MJ/l) of liquid DME is relatively low, about half that of diesel fuel, so adjustment of the fuel injection duration is needed for conversion to DME.

F–T synthetic diesel fuel is produced from a mixture of carbon monoxide and hydrogen gas using a high-temperature gas to liquid catalytic reforming process. It is a polymerization process resulting in long straight-chain hydrocarbon alkanes. A variety of catalysts can be used, but the most commonly used are cobalt, iron, and ruthenium.

The F–T reaction is:

$$n\mathrm{CO} + (2n+1)\mathrm{H_2} \longrightarrow C_nH_{2n+2} + n\mathrm{H_2O} \tag{1.4}$$

The F–T process was first developed by two German scientists, Franz Fischer and Hans Tropsch, in 1925. The source CO is generated by pyrolysis of coal or woody materials, such as switchgrass. The F–T process has been successfully scaled up and used in large-scale natural gas-to-liquid and coal-to-liquid facilities worldwide. It is also used in CO_2 capture schemes, in conjunction with a reverse water–gas reaction.

1.7.13 Cetane Number

The standard measure of the autoignition characteristics of compression ignition fuels is the cetane number *CN*. It is a dimensionless number with a scale that varies from 15 to 100. The upper and lower limits of the cetane number are defined by two primary alkane reference fuels. The upper reference fuel is *n*-cetane (hexadecane), an unbranched $C_{16}H_{34}$, with a reference cetane value of 100. The lower reference fuel is an isomer *iso*-cetane (heptamethylnonane), a highly branched $C_{16}H_{34}$, with a reference cetane value of 15. Additives such as nitrate esters, for example, 2-ethyl hexyl nitrate, can be used to increase the cetane number. The cetane number is measured using a standard Waukesha CFR research engine with a pre-chamber and a variable compression ratio. The cetane number *CN* and the octane number *ON* are inversely correlated, as gasoline is a poor diesel fuel and vice versa.

1.8 Fuels for Rocket Engines

Rocket engines are propulsion devices that carry their own fuel and oxidizer and do not need air for combustion. A comparative measure of different rocket fuels is the specific impulse I_{sp}, defined as the thrust T per unit weight flow, $\dot{m}g$, with units of seconds. The specific impulse indicates for how long a time that engine can exert a continuous force, i.e., thrust, until fully burning the propellant mass. Historically, the first rockets used solid propellants, such as gunpowder. R. Goddard (1882–1945), an American engineer, built the first liquid-fueled rocket in 1926, using gasoline and liquid oxygen (LOX). Kerosene has also been used as a rocket fuel with LOX as the oxidizer. Similar rocket fuel research was conducted at the same time in Russia by K. Tsiolkovsky (1857–1935) and in Germany by H. Oberth (1894–1989).

1.8.1 Cryogenic Fuels

A cryogenic fuel is one that is at a temperature less than $T = 183\,\text{K}$ ($-90\,^\circ\text{C}$). Cryogenic fuels include liquid hydrogen (LH_2) at $T = 20\,\text{K}$ and liquid methane at $T = 100\,\text{K}$. LOX at 50–90 K is used as the oxidizer. Liquid hydrogen fuel has a very high specific impulse of 450 seconds. These cryogenic mixtures require a spark for initial ignition.

1.8.2 Hypergolic Propellants

Hypergolic propellants are fuels that ignite upon contact with one another. An example of a hypergolic rocket fuel is monomethylhydrazine (MMH) CH_3NHNH_2 with the oxidizer nitrogen tetroxide N_2O_4. The specific impulse of hypergolic fuels ranges from 260 to 310 seconds. Rocket engines with hypergolic fuels are usually simple and reliable because they need no ignition system. The most common hypergolic fuels are in a liquid state at ambient temperatures and pressures. The corrosivity, toxicity, and carcinogenicity of traditional hypergolic fuel require extensive safety precautions.

1.8.3 Solid Propellants

With solid propellants, the fuel and oxidizer are premixed and cast in solid form. An example of a solid propellant is a mixture of aluminum powder as a fuel and ammonium perchlorate NH_4ClO_4 as an oxidizer. The specific impulse of solid propellants ranges from 200 to 300 seconds. The combustion process is dependent on the surface area of the fuel. Once ignited, a solid propellant will burn to completion, so it is difficult to throttle a solid propellant for rocket thrust control.

1.9 Solid Fuels

The two main categories of solid fuels are biomass and coal. Biomass, a renewable organic material, includes wood, agricultural residues, and organic waste, with the largest biomass energy source being wood. Coal is the solid fossilized residue of plant biomass, with common varieties such as lignite, bituminous, and anthracite coal.

Wood has a complex heterogeneous cellular structure and is composed of three main components: cellulose, hemicellulose, and lignin. The main component of wood is cellulose, which is often used as a surrogate for biomass. The inner cavity of a wood cell is called the lumen, and the surrounding structural layer is the cell wall, which consists mainly of cellulose. Cellulose is a carbohydrate polymer composed of long linear chains of glucose ($C_6H_{12}O_6$) units linked by β-1,4-glycosidic bonds. Hemicellulose is also a carbohydrate polymer, shorter in length than cellulose, with an amorphous branched structure, and is located between the cellulose and lignin. Lignin is a polymer composed mainly of linked phenylpropane ($C_6H_5CH_2\ CH{=}CH_2$) units which hold the cellulose structure together.

Coal is primarily composed of carbon with variable amounts of other elements such as hydrogen, sulfur, oxygen, and nitrogen. During the fossilization or coalification process, the hydrocarbon aliphatic chains are replaced by aromatic rings, which then fuse into polyaromatic linked rings, with a corresponding increase in the percentage of carbon and decrease in the percentage of hydrogen and oxygen, as indicated in Table 1.5. Coal is classified in terms of rank and grade. The rank is a measure of the carbon content and heating value. In increasing rank are lignite,

Table 1.5 Comparison of Representative Wood and Coal Components and Heating Value (Dry, Ash-free).

	Fir	Pine	Anthracite Coal	Bituminous Coal
Proximate analysis (wt%)				
Volatile matter	86.2	87.0	6.4	17.7
Fixed carbon	13.7	12.8	81.4	71.9
Ultimate analysis (wt%)				
Carbon	52.3	59.0	82.1	80.1
Hydrogen	6.3	7.2	2.3	4.3
Oxygen	40.5	32.7	2.0	2.2
Nitrogen	0.1	—	0.8	1.3
Sulfur	—	—	0.6	1.7
Ash	0.8	1.1	12.2	10.4
Higher heating value q_c (MJ/kg)	21.5	24.2	30.8	32.5

Source: Adapted from Tillman et al. (1981).

bituminous, and anthracite coal. The grade indicates the quality of the coal, which depends on the ash and sulfur content.

In recent years, coal has supplied about a quarter of the world's primary energy. However, the CO_2 emissions from the combustion of coal since the advent of the Industrial Revolution have been the major contributor to global climate change, leading many countries to reduce or eliminate their use of coal. The CO_2 generated by biomass combustion is eventually recycled back to biomass through photosynthesis. Therefore, renewable fuels such as biomass can be CO_2 neutral if sourced using sustainable cultivation practices.

The composition of solid fuels is reported with a proximate analysis or an ultimate analysis. Proximate analysis is a standardized method to determine the moisture, volatile matter, char, and ash content of a given solid fuel. Volatile matter is defined as the volatile gases that are produced and driven off by heating the solid fuel. The volatile gases burn more rapidly than the remaining char particles and contribute to flame ignition and stability. Char is a measure of the amount of nonvolatile carbon remaining in a sample. Ash is the assortment of oxidized inorganic mineral compounds remaining after the combustion process is complete. An ultimate analysis is a standardized method which provides the chemical element composition of a solid fuel, namely, the molecular carbon, hydrogen, nitrogen, oxygen, and sulfur content, and is reported on a dry, ash-free weight percent basis.

The analysis procedures for the proximate analysis, ultimate analysis, and heating value of wood are given in ASTM E870, and the procedures for the proximate and the ultimate analysis of coal are given in ASTM D3172 and ASTM D3176, respectively. With the ASTM D3172 proximate analysis procedure, a sample of coal is crushed and dried in an oven at 105–110 °C to determine residual moisture. The sample is then heated in a covered crucible at 900 °C to a constant weight. This weight loss is the volatile matter. The remaining sample is then placed in an oven at 750 °C with the crucible cover removed to allow the sample to combust. The weight loss on completion of combustion is termed fixed carbon or char. The remaining residue is defined as ash. For ultimate analysis procedure, a coal sample is combusted in an elemental analyzer, which measures the weight percent of the elements carbon, hydrogen, nitrogen, sulfur, and ash. The oxygen percentage is determined by the remaining percentage.

Representative compositions of the softwoods fir and pine, anthracite coal, and bituminous coal are compared in Table 1.5. Wood has about 60–70% of the heating value of coal. Wood has substantially more volatile matter while having less fixed carbon than coal, so that about 60% of the heating value of wood is produced by the volatile matter. The large amount of volatile matter associated with wood is a result of the high number of functional groups (alkanes, etc.) and the low number of aromatic structures in the wood. The mass hydrogen/carbon ratio H/C of the softwood fir is about 0.12, and bituminous coal has a mass H/C ratio = 0.054. Coal also has substantially larger amounts of sulfur and nitrogen, which create environmental issues.

Wood is classified as either a hardwood or softwood, each having different physical structures. Hardwoods are deciduous trees such as maple, oak, and cherry. Softwoods are generally conifers such as pine, cedar, and fir trees. The primary distinguishing feature between softwoods and hardwoods is that hardwoods, such as oak and teak, have pores that transport water throughout the wood. The dry, ash-free high heating value (q_c) of hardwoods ranges from 19 to 21 MJ/kg and that of softwoods ranges slightly greater at 20–22 MJ/kg. Hardwoods generally have a higher density, higher hemicellulose, and a lower lignin content, and sometimes a slightly higher cellulose content.

Wood and coal are hygroscopic and absorb water, which is contained in both free and bound form. Free water is water that is absorbed by capillary uptake and resides in the wood or coal pores. Bound water is water that is adsorbed into the wood or coal cell wall, and is held by hydrogen bonds. Adsorption is characterized by the release of thermal energy due to the formation of hydrogen

bonds and the interaction of Van der Waal's forces. Therefore, the heating value of a given wood species is strongly dependent on its free and bound water content. As such, the energy required to dry a given species of wood depends on the energy needed to heat the wood and the subcooled water to 373 K, the heat of vaporization (∼ 2400 kJ/kg) of the free water, and the heat of sorption (∼200–300 kJ/kg)of the bound water, all of which also affect the rate of combustion. The moisture content of wood can range from 5% for dried wood to 50% for green wood.

The composition of solid fuels is reported in three ways, as-received (ar), dry (d), or dry, ash-free (daf). The as-received composition is therefore

$$m_{\text{ar}} = m_{\text{daf}} + m_w + m_{\text{ash}} \tag{1.5}$$

where m_w is the mass of water and m_{ash} is the mass of ash in the fuel. The heating value of the fuel q_c will be reduced when the non-combusting moisture and ash in the fuel is accounted for:

$$q_{c,\text{ar}} = q_{c,\text{daf}} \frac{m_{\text{daf}}}{m_{\text{ar}}} \tag{1.6}$$

Example 1.4 ***Solid Fuel Heating Value***

From proximate analysis, a sample of pinewood has 25% moisture, 6% ash, and a high heating value of 20 MJ/kg on a dry, ash-free basis. What is the high heating value of an as-received (ar) basis?

Solution

The as-received mass m_{ar} is

$$\begin{aligned} m_{\text{ar}} &= m_{\text{daf}} + m_w + m_{\text{ash}} \\ &= m_{\text{daf}} + 0.25\, m_{\text{daf}} + 0.06\, m_{\text{daf}} \\ &= 1.31\, m_{\text{daf}} \end{aligned}$$

The heating value on an as-received basis is

$$\begin{aligned} q_{c,\text{ar}} &= q_{c,\text{daf}} \frac{m_{\text{daf}}}{m_{\text{ar}}} \\ &= 20\, \frac{m_{\text{daf}}}{1.31\, m_{\text{daf}}} \\ &= 15.3\,\text{MJ/kg} \end{aligned}$$

1.10 Additional Reading

The references at the end of this introductory chapter contain a listing of both past and current books that will provide further information about both combustion science and engineering. These sources will give the reader a deeper appreciation of how our understanding and modeling of combustion processes has advanced in the last 50 years. In chronological order, these books are Kanury (1975), Gaydon et al. (1979), Williams (1985), Lewis and von Elbe (1987), Linan and Williams (1994), Fristrom (1995), Drysdale (1999), Law (2006), Warnatz et al. (2006), McAllister et al. (2011), Kuo and Acharya (2012), Glassman et al. (2014), Turns and Haworth (2020), Kirkpatrick (2021), Poinsot and Veynante (2022), and Bryden et al. (2022).

In addition, scholarly journals including

Combustion and Flame,
Combustion Science and Technology,
Journal of Chemical Physics,

Journal of Physical Chemistry,
Journal of Propulsion and Power,
Progress in Energy and Combustion Science, and
Proceedings of the Combustion Institute

provide up to date research findings in the various combustion areas.

References

Bryden, K., K. Ragland, and S. Kong (2022), *Combustion Engineering*, CRC Press, Boca Raton, FL.
Drysdale, D. (1999), *An Introduction to Fire Dynamics*, 2nd ed., John Wiley and Sons, New York.
Fristrom, R. (1995), *Flame Structure and Processes*, Oxford University Press, New York.
Gaydon, A., H. Wolfhard, and S. Penner (1979), *Flames, Their Structure, Radiation and Temperature*, 4th ed., Chapman and Hall, London, England.
Glassman I., R. Yetter, and N. Glumac (2014), *Combustion*, 5th ed., Academic Press. Cambridge, MA.
Kanury A. (1975), *Introduction to Combustion Phenomena*, Gordon and Breach, New York.
Kirkpatrick, A. (2021), *Internal Combustion Engines: Applied Thermosciences*, 4th ed., John Wiley and Sons, New York.
Kuo, K. and R. Acharya (2012), *Fundamentals of Turbulent and Multiphase Combustion*, John Wiley and Sons, New York.
Law, C. K. (2006), *Combustion Physics*, Cambridge University Press, New York.
Lewis, G. and B. von Elbe (1987), *Combustion, Flames, and Explosions of Gases*, 3rd ed., Elsevier, New York.
Linan, A. and F. Williams (1994), *Fundamental Aspects of Combustion*, Oxford University Press, Oxford, UK.
Malenshek, M. and D. Olsen (2009), Methane number testing of alternative gaseous fuels, *Fuel*, Vol. 88, pp. 650–656.
McAllister, S., J. Chen, and A. Fernandez-Pello (2011), *Fundamentals of Combustion Processes*, Springer, New York.
Owen, K. and T. Coley (1995), *Automotive Fuels Reference Book*, Society of Automotive Engineers, Warrendale, PA.
Poinsot, T. and D. Veynante (2022), *Theoretical and Numerical Combustion*, 3rd ed., CNRS.
Smil, V. (2017), *Energy Transitions: Global and National Perspectives*, Praeger, Santa Barbara, CA.
Tillman, D. A., A. J. Rossi, and W. D. Kitto (1981), *Wood Combustion-Principles, Processes, and Economics*, Academic Press, New York.
Turns, S. and D. Haworth (2020), *An Introduction to Combustion*, McGraw-Hill, New York.
Warnatz, J., U. Maas, and R. Dibble (2006), *Combustion*, Springer-Verlag, Berlin, Germany.
Williams, F. (1985), *Combustion Theory*, 2nd ed., CRC Press, Boca Raton, FL.

Homework Problems

1.1 What is the chemical structure of 2,4-diethylpentane?

1.2 What is the chemical structure of (a) *n*-hexane, (b) methylnaphthalene, and (c) heptamethylnonane?

1.3 An internal combustion engine fuel is a mixture of 70% octane and 30% nitromethane, by volume. What should the mass air–fuel ratio be to run rich at an equivalence ratio $\phi = 1.24$?

1.4 If a hydrocarbon fuel is represented by the general formula C_xH_{2x}, what is its stoichiometric mass air–fuel ratio?

1.5 A fuel has the following composition by mass: 10% pentane, 35% heptane, 30% octane, and 25% dodecane. If its general formula is of the form C_xH_y, (a) find x and y; (b) What is its stoichiometric combustion equation?

1.6 What is the percentage difference in the heat of combustion for methanol when used as a liquid at 25 °C and when used as a vapor at 25 °C? (Hint: Review Tables 2.1 and 2.9.)

1.7 What are the normalized CO_2 emissions (g_{CO_2}/MJ_{fuel}) resulting from the stoichiometric combustion of propane, methane, methanol, ethanol, and gasoline?

1.8 Pinewood has a high heating value (ash-free dry basis) of 24.2 MJ/kg. What is the ash-free high heating value and lower heating value as a function of moisture content at 0, 20, 40, and 60%?