SAND2012-9826P

Fuels and the Impact of Fuel Composition on Engine Performance

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1. INTRODUCTION

The chemical composition of a fuel determines its properties, and the properties of a fuel determine its engine-performance characteristics. Historically, the liquid-phase hydrocarbon fuels used for transportation and non-road applications have been refined from crude petroleum recovered from beneath the surface of the Earth. Hydrocarbons are compounds that contain only the elements hydrogen and carbon. A compound is defined as a pure chemical substance composed of two or more elements bonded in a specific structural arrangement and exhibiting fixed ratios of the different elements. The word "petroleum" is derived from Latin roots; its literal translation is "rock oil."

As supplies of readily accessible conventional petroleum have been consumed, the cost of petroleum production has increased, and environmental and political concerns related to petroleum use have grown. This trend has intensified interest in "renewable" fuels that are currently created from biomass, and in the future might be created directly from solar energy. Renewable fuels can be beneficial from a greenhouse-gas (GHG) perspective because they essentially recycle carbon dioxide (CO_2, a GHG) from the atmosphere. For example, plants absorb carbon in the form of atmospheric CO_2 as they grow, which offsets the CO_2 released when fuels made from plants are burned. From a GHG perspective, this is preferable to continuing to convert petroleum-carbon into new atmospheric CO_2. Although the histories of renewable fuels are significantly different from those of petroleum fuels, renewable fuels can contain many of the same kinds of chemical structures found in petroleum-based fuels, depending on how they are made. One notable difference is that some common renewable fuels on the market today are oxygenates, i.e., compounds that contain oxygen as well as hydrogen and carbon.

Liquids composed primarily of hydrogen, carbon, and perhaps some oxygen are fuels of choice for transportation applications due to the high amounts of energy they contain per unit mass (specific energy) and per unit volume (energy density). For example, the specific energy of diesel fuel is approximately an order of magnitude larger than that of dynamite. This is primarily because effectively the entire mass of diesel fuel is fuel elements, while the mass of an explosive like dynamite includes the mass of oxidizer as well as fuel elements, and the oxidizer does not carry any extra energy. The specific energies of liquid hydrocarbon fuels also are many times larger than those of advanced batteries. This high specific energy means that only a small mass of fuel needs to be carried aboard a vehicle or machine to produce a large amount of useful mechanical work. For at least a century, the reciprocating internal-combustion engine has been the device of choice for converting the chemical energy stored in liquid fuels into mechanical work for ground-transportation and non-road applications.

Currently, reciprocating internal-combustion engines for passenger-car and commercial applications fall into either of two broad categories: spark-ignition (SI) engines or compression-ignition (CI) engines. SI engines tend to be used in light-duty applications (e.g., passenger cars) because they are less expensive, quieter, and have lower exhaust emissions (thanks to the highly efficient three-way catalyst [1]) than their CI counterparts. CI engines tend to be used in heavy-duty applications (e.g., truck, rail, and marine transportation) due to their higher efficiencies (i.e., lower fuel costs), better durabilities, and improved low-speed torque capabilities.

The specific effects of changing a given fuel property depend upon many detailed parameters of the engine in which the fuel is used and the conditions over which the engine is operated. The fuel properties required for robust operation of SI and CI engines are different; as a result, different fuels have evolved for use with these different engines. SI engines typically burn gasoline, while CI engines typically burn diesel fuel. The primary differences between gasolines and diesel fuels are that gasolines are resistant to autoignition and are more volatile (i.e., require less energy for vaporization and have lower boiling temperatures), while diesel fuels readily autoignite and are less volatile.

Covering all aspects of fuels for reciprocating internal-combustion engines and the impact of fuel composition on engine performance in a single article of reasonable length is impossible. Hence, the objective of this document is to give the reader a broad overview of the relevant fuel science and a flavor of the key issues, while going into detail in selected areas of particular importance. The article starts with a discussion of fuel-production techniques and fuel compositional attributes, followed by an overview of fuel properties that affect end-use characteristics, and a discussion of the fuel specifications developed to ensure that fuels perform as required in their applications. The article concludes by summarizing the main points and offering some thoughts on what the future might hold for fuels and reciprocating internal-combustion engines.

2. FUEL PRODUCTION

Fuels and fuel components can be produced from a wide variety of feedstocks, including: crude oil, oil sands, natural gas, biomass, coal, oil shale, methane hydrates, and even carbon oxides (CO, CO_2) reacted with hydrogen. This section reviews the primary fuel-production pathways currently in use.

The huge scale of fuel production is a key factor to keep in mind when evaluating conventional and alternative technologies. In 2011, global oil consumption was ~88 million barrels per day [2], and US consumption was ~19 million barrels per day [3]. At 42 US gallons per barrel, global oil consumption is ~3.7 billion gallons per day, or nearly four Olympic-sized swimming pools per minute, representing a market value of ~$9 billion per day at the present crude-oil cost of ~$100/barrel. The majority of this oil is used to produce transportation fuels, with the balance used for heating oil and industrial processes.

2.1. Crude Oil Refining

The vast majority of the liquid hydrocarbon components of fuels today are produced from petroleum-derived crude oil. Crude oils from different geographic locations and production processes can have a wide range of properties: from low densities and viscosities (referred to as "light"), to high densities and viscosities similar to tar ("heavy"); and from low sulfur ("sweet") to high sulfur ("sour"). All crude oils are primarily composed of hydrocarbons of the alkane and aromatic classes (see Section 3).

Refining is the process of converting crude oil into higher-value products, including fuels for reciprocating internal-combustion engines. A typical modern refinery is a complex combination of interdependent processes that can be divided into three basic categories: separation, upgrading, and conversion [4,5].

Distillation is the most important and widely used separation process in a refinery. Distillation is a process at the front end of a refinery that divides crude oil into different boiling fractions. Petroleum fractions that undergo little or no processing beyond distillation are called "straight-run" products. In the early days of petroleum refining, when fuel demand was low, engines had low compression ratios, and sulfur specifications were non-existent, refineries produced mostly straight-run products, but today significant further processing of the individual fractions is typically necessary to provide the required fuel properties.

Upgrading processes remove undesirable impurities such as sulfur, nitrogen, and metal compounds. For example, bitumen (the tar-like hydrocarbon derived from oil sands and a key feedstock for fuels in North America) requires extensive upgrading, after which it becomes "synthetic crude" that can be processed in a conventional refinery [6]. The most-common upgrading techniques in use today involve hydrotreating, a broad class of strategies involving reactions of fuel species with hydrogen in the presence of a catalyst, usually at conditions of elevated temperature and pressure.

Conversion processes are used to enable the refinery to produce fuels meeting specifications in quantities that match the market demand. One class of conversion processes is cracking. Conversion processes such as fluid catalytic cracking (FCC) and hydrocracking are used to lower ("crack") the molecular weights of the heavier fractions from the distillation column to those appropriate for the various fuel classes. Other conversion processes such as reforming and alkylation increase the octane number to levels suitable for gasoline by producing aromatics and branched alkanes, respectively.

Base fuels are produced by blending various intermediate streams in the correct proportions at the refinery. Other components can be blended into a base fuel at a pipeline or rail terminal downstream of the refinery. The blending of additives and/or other components (e.g., ethanol or biodiesel) results in finished fuels, which are subsequently distributed to their various points of sale.

2.2. Fischer-Tropsch Type Processes

Another method of producing fuel components is to synthesize them from a mixture of carbon monoxide (CO) and molecular hydrogen (H_2) called "synthesis gas" in a polymerization-type process that makes CH_2 (methylene) building blocks for hydrocarbons plus water (H_2O) as a by-product:

$$nCO + 2nH_2 \rightarrow -(CH_2)_n- + nH_2O \qquad (2.1)$$

The process name is derived from two German researchers who discovered effective catalysts and operating conditions to facilitate the reaction in Eq. 2.1. Depending on the specific catalysts and reaction conditions used, oxygenates also can be produced by Fischer-Tropsch (or simply F-T) synthesis. Feedstocks that can be used to make synthesis gas include coal, natural gas, and biomass. Germany commercialized the process using coal to produce fuels during World War II. In South Africa during an oil embargo in the 1970s, Sasol made further technology developments and built plants to produce fuels from coal, which remain operational today. Several plants have recently been built in which natural gas is the feedstock that is converted to the synthesis gas. Diesel fuel production is maximized by operating at lower temperatures that favor the creation of waxy, long-chain, normal alkanes, and subsequently cracking the chains into the diesel range. To improve the cold-temperature properties of the diesel fuel, the normal alkanes are "isomerized" to produce branched alkanes (see Section 3.1.2). The resulting product has a high cetane number (70+), but the near-zero aromatic content can cause leakage issues for the elastomeric seals present in some engines/vehicles that require polar compounds in the fuel to enable the seals to swell to form a tight fit (see Section 4.4.2). Capital costs for Fischer-Tropsch plants tend to be fairly high, primarily due to the costs of the synthesis-gas plants, and fuels produced from those processes are only economically viable if there is long-term availability of a large source of extremely low-cost feedstock.

2.3. Natural Gas and Liquefied Petroleum Gas

Natural gas and liquefied petroleum gas (LPG) are lighter petroleum-derived products. Natural gas can be used in compressed (CNG) or liquefied (LNG) forms. Compared to gasoline, these fuels have higher octane and their combustion products have lower GHG footprints. A principal component of natural gas is methane, however, and any leaked methane will have a GHG potential 21 times higher than that of CO_2. Although the lower energy densities of CNG, LNG, and LPG tend to limit the range of vehicles in which they are employed, these fuels are used in a number of Asian, South American, and European countries. In the US, the larger personal vehicles and the limited distribution infrastructure for highly volatile fuels have largely restricted the use of CNG, LNG, and LPG to fleets with centralized refueling facilities. Nevertheless, the growing amounts of recoverable shale gas in some countries, and the corresponding decreased costs of natural gas and light condensed liquids relative to gasoline and diesel fuel, may lead to the wider use of these fuels in the future [7].

2.4. Biomass

2.4.1. Ethanol Production

Ethanol is currently added to most of the gasoline sold in the US and in many countries around the world. It is predominantly produced by fermentation [8], and the primary feedstocks for ethanol production are the starches and sugars in crops such as corn, sugar beets, and sugar cane. The issue of whether food crops should be used to make fuel components (see Section 4.5.4) and the limited life-cycle GHG-reduction benefits of corn-based ethanol (see Ch. 4 of [8]) have led to a significant amount of research and development on the conversion to ethanol of cellulosic materials found in sources such as wood and fast-growing non-food crops like switchgrass. Commercial production of ethanol from cellulosic material is presently negligible, however, relative to ethanol production from starches and sugars.

2.4.2. Biodiesel Production

Biodiesel is an oxygenated bio-derived product composed of fatty acid methyl esters (FAMEs). Esters have the general structure R-(C=O)O-R’, where R and R’ signify hydrocarbon chains. Typically, the R group is a straight hydrocarbon chain with five to 21 carbon atoms and containing zero to three carbon-carbon double bonds (i.e., the chain can be unsaturated, see Section 3.1.3). In the transesterification reactions that create biodiesel, the R-(C=O)O structures come from vegetable- or animal-derived triglycerides (or fatty acids), and the R’ comes from an alcohol, as shown in Fig. 2.1. The alcohol used in the reaction is commonly methanol, though sometimes ethanol or higher alcohols are used. Hence, methyl esters are produced when methanol is used in the transesterification reaction, ethyl esters are produced when ethanol is used, and so on. The most common source of triglycerides for biodiesel in the US is soybean-derived vegetable oil.

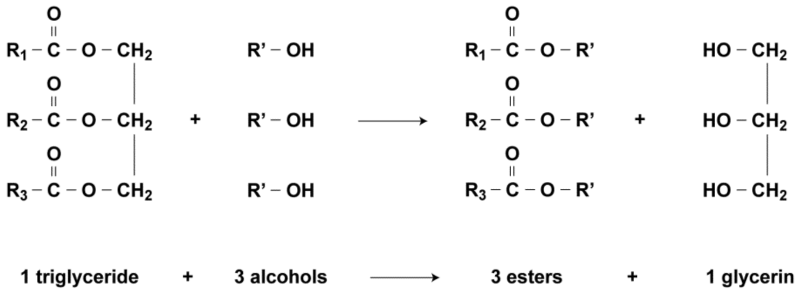


Figure 2.1. The transesterification reaction used to produce biodiesel esters (the reaction typically employs a catalyst).

2.4.3. Renewable Diesel Production

One alternative to reduce or eliminate many of the issues discussed above for biodiesel is to catalytically react the triglycerides with hydrogen instead of alcohols to produce alkane molecules that are essentially identical to, and completely fungible with, conventional petroleum-derived diesel. The hydroprocessing techniques required to produce these products are very similar to those currently used by refineries to upgrade crude oil, so conceivably these bio-derived feedstocks could be co-processed with crude oil in refineries.

2.4.4. Other Biofuel Production Approaches

A number of other possible paths are being explored to convert biomass to transportation fuels, and these can be grouped into two broad categories: thermochemical and biochemical. Thermochemical routes typically employ elevated temperatures (and/or pressures) as well as catalysts. Thermochemical routes such as pyrolysis (reactions occurring at elevated temperature, reduced oxygen content, and perhaps in the presence of catalysts) can convert even solid-phase biomass to liquids, but these liquids can require significant post-processing [9] before being suitable for use in modern engines [10]. Another thermochemical route, gasification, can be used to convert organic feedstocks to synthesis gas that can then be burned directly in engines or converted to liquid hydrocarbons through the Fischer-Tropsch process (see Section 2.2).

Biochemical routes involve using micro-organisms to produce fuels directly, or using micro-organisms or their enzymes to break down biopolymers such as cellulose, hemicellulose, and lignin, as intermediate steps in the fuel-production process. Examples include the direct production of hydrocarbons by *Botryococcus braunii* [11], methane production via anaerobic digestion, and conventional and cellulosic ethanol production processes via fermentation (see Section 2.4.1).

3. FUEL COMPOSITION

Because the chemical composition of a fuel determines its properties, it is helpful to have some knowledge of the types of compounds found in modern fuels. Modern gasolines and diesel fuels have a high degree of compositional complexity, with typical fuel samples containing over 100 and 1000 distinct compounds, respectively. The compounds present in greatest abundance in current fuels are hydrocarbons and oxygenates, but trace components also are present, and they can have strong effects on engine performance. These three classes of fuel constituents are introduced in the context of liquid-phase fuels and discussed below. The section concludes with a brief discussion of the composition of gaseous fuels.

3.1. Hydrocarbons

Crude petroleum and the fuels derived therefrom typically contain five classes of hydrocarbon compounds: unbranched alkanes, branched alkanes, cyclic alkanes, olefins, and aromatics. The relative concentrations of the different hydrocarbon classes in a given fuel are a function of the feedstocks and processing strategies employed in its production.

The total number of carbon atoms in a compound is known as its carbon number, denoted n. A representative molecule from each hydrocarbon class having n = 8 is shown in Fig. 3.1 using several common notational conventions. All elements are shown in the condensed structural formula for n-octane and the dash structural formulas for the other hydrocarbons in Fig. 3.1. In contrast, only carbon bonds are shown in the bond-line structural formulas. In this latter notation, a carbon atom is assumed to exist at the end of each straight-line segment (unless the symbol of a different element is shown in its place), hydrogen atoms are not shown, two parallel line segments indicate a double bond between adjacent atoms, and a hexagon with a circle inside it indicates a benzene ring.

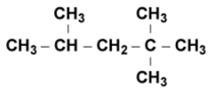
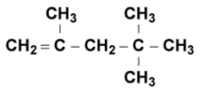
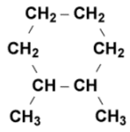
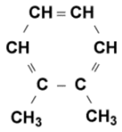
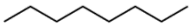
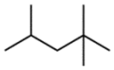
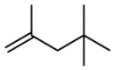
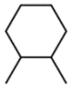
Hydrocarbon Class	**Unbranched Alkane**	**Branched Alkane**	**Olefin**	**Cyclic Alkane**	**Aromatic**
Representative Compound	n-octane	2,2,4-trimethyl-pentane (iso-octane)	2,4,4-trimethyl-1-pentene	trans-1,2-dimethyl-cyclohexane	1,2-dimethyl-benzene (ortho-xylene)
Chemical Formula	C_8H_{18}	C_8H_{18}	C_8H_{16}	C_8H_{16}	C_8H_{10}
Condensed or Dash Structural Formula	$CH_3(CH_2)_6CH_3$	 $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_3$	 $CH_2=\overset{\overset{CH_3}{\vert}}{C}-CH_2-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_3$		
Bond-line Structural Formula					

Figure 3.1. Representative molecules from the five hydrocarbon classes with carbon number n = 8. Molecules within the gasoline boiling range were selected for simplicity.

Different compounds with the same chemical formula are called isomers. As shown in Fig. 3.1, n-octane and iso-octane are isomers, as are 2,4,4-trimethyl-1-pentene and trans-1,2,-dimethylcyclohexane. These types of isomers, i.e., those that differ in the sequences in which their atoms are arranged, are called constitutional isomers. Other types of isomerism exist, such as stereoisomerism, as discussed in the subsection on cyclic alkanes below. Isomerism is an important concept in fuel science because different isomers can have starkly different physical and chemical properties.

3.1.1. Unbranched Alkanes

Also sometimes known as normal alkanes, n-alkanes, or n-paraffins, these “straight-chain” hydrocarbons have only single bonds between their carbon atoms, and their carbon atoms are all positioned along a single zig-zagging but roughly linear chain (see the bond-line structural representation of n-octane in Fig. 3.1). Their chemical formulas are of the form C_nH_{2n+2}, where n is the carbon number of the molecule. Unbranched alkanes are called saturated compounds because they contain the maximum possible number of hydrogen atoms for their given number of carbon atoms and general structure.

3.1.2. Branched Alkanes

These branched-chain hydrocarbons are also commonly known as iso-alkanes or iso-paraffins (though technically the term “iso-alkane” refers only to an alkane with a single methyl group attached to the second carbon atom of its primary chain). Like unbranched alkanes, the branched alkanes are saturated hydrocarbons with chemical formulas of the form C_nH_{2n+2}, but the carbon atoms are no longer all arranged along a single linear chain. Instead there are one or more alkyl branches extending from the main hydrocarbon chain. For example, Fig. 3.1 shows that iso-octane has three methyl branches, two from the second carbon atom of the main pentane chain, and one from the fourth.

3.1.3. Olefins

Also sometimes known as alkenes, olefins are hydrocarbons that contain at least one carbon-carbon double bond. Olefins can exist as unbranched, branched, or cyclic structures. The olefin shown in Fig. 3.1 has a branched structure with the double bond between the carbon atoms in the first and second positions. An olefin is an unsaturated compound because hydrogen atoms can be added to it without changing the general arrangement of its carbon atoms. For example, the olefin shown in Fig. 3.1 could be converted to iso-octane by the addition of two hydrogen atoms. Although olefins are not typically found in crude petroleum in high concentrations, they can be produced during gasoline refining (e.g., via thermal cracking).

3.1.4. Cyclic Alkanes

Also called cyclo-alkanes or naphthenes, cyclic alkanes are saturated compounds with their carbon atoms arranged in one or more ring structures. Cyclo-alkanes may have three to nine carbon atoms in each ring structure, where the chemical formula of a single-ring cyclo-alkane is C_nH_{2n}. Five- and six-membered rings are the most stable (and hence the most abundant in petroleum-derived fuels) due to their lower carbon-bond strains. The carbon atoms in cyclo-alkane rings are not co-planar. In a five-carbon ring, one of the carbon atoms is raised above the plane of the other four. In a six-carbon ring, a number of conformations are possible, with the two most common being the “chair” and “boat” conformations. These two different conformations of cyclohexane are illustrated in Fig. 3.2.

Figure 3.2. Conformations of cyclohexane: **a**. chair; **b**. boat.

In these conformations, four of the carbon atoms are co-planar, while the remaining two either lie on different sides of the plane (the chair conformation, which is the most stable), or on the same side of the plane (the boat conformation). The potential-energy differences among the different cyclohexane conformations are low enough that the molecule can change conformations (or “interconvert”) approximately 1 million times per second at standard conditions [12]. These and other conformational differences among molecules can lead to stereoisomerism, i.e., molecules with the same chemical formula but different arrangements of their atoms in space that will not interconvert at standard conditions. Cyclo-alkanes with one or more unbranched or branched side chains, called substituents, are common and may exhibit stereoisomerism. When the substituents both project above the nominal plane of the cyclohexane ring, the compound is a cis isomer; when one substituent projects above and one below, the compound is a trans isomer. For example, the trans-1,2-dimethylcyclohexane shown in Fig. 3.1 has methyl substituents bonded to the carbon atoms in the 1 and 2 positions on the ring, with one projecting above the nominal plane of the cyclohexane ring and one below.

3.1.5. Aromatics

Aromatics are unsaturated compounds with their carbon atoms arranged in one or more ring structures. The most common aromatic hydrocarbons are those containing one or more benzene rings. A benzene ring has the formula C_6H_6. In contrast to cyclohexane, all six carbon atoms in a benzene ring lie in the same plane. The benzene rings in fuel-derived aromatic compounds can and often do have one or more alkyl substituents.

3.2. Oxygenates

The second-most-abundant class of compounds found in modern fuels is oxygenates. These are compounds composed not just of hydrogen and carbon, but also of oxygen. The oxygenate classes most commonly used in fuels today are alcohols and esters, though other classes also have been and are used. Some common types of oxygenates are discussed below.

3.2.1. Alcohols

Alcohols have the general formula R-O-H, where R signifies a hydrocarbon radical. Hence, the alcohol formed from the ethyl radical (C_2H_5) is ethyl alcohol, which is also known as ethanol (C_2H_5OH). Ethanol is produced by fermentation, and is by far the most commonly used oxygenate in gasolines, with nearly all gasoline sold in the US currently containing some ethanol. Higher alcohols such as butanol isomers also are potential high-octane bio-derived alcohol blendstocks for gasoline, and methods for scaling up their production are under development.

3.2.2. Esters

Esters have the general structure R-(C=O)O-R’, where R and R’ signify hydrocarbon radicals. Esters are discussed in Section 2.4.2 on biodiesel production. Although esters most commonly enter fuels as biodiesel FAMEs, they also can be derived directly from various biological and other processes. Raw vegetable- or animal-derived lipids, however, typically are not esters. They are triglycerides and/or fatty acids.

3.2.3. Ethers

Ethers have the general structure R-O-R’, where again R and R’ denote hydrocarbon radicals that may be different. The most well-known fuel ether is methyl tert-butyl ether (MTBE), which was approved for use at levels up to 15 vol% in gasoline by the US EPA in the 1980s and added to Federal and California reformulated gasolines. This use was banned in California and a number of other states in 2004, after MTBE was found in certain drinking-water supplies. Some humans can taste MTBE at concentrations below 0.1 parts per million (ppm) [13]. Despite the US experience with MTBE, some countries continue to allow the use of MTBE in gasoline. Other ethers show some promise as additives for diesel fuel, because their oxygen content is beneficial for lowering soot emissions, and they can have cetane numbers > 60 [14].

3.2.4. Ketones

Ketones have the general structure R-(C=O)-R'. A common ketone is the solvent acetone, or dimethyl ketone: $CH_3(C=O)CH_3$. Ketones are not found in current fuels in high concentrations, but they can be produced efficiently by biological processes and hence may be important components of future biofuels.

3.3. Trace Components

While trace components are, by definition, minor fuel constituents, they can have profound effects on engine performance through a number of mechanisms. These mechanisms include but are not limited to:

- Corrosion of fuel-system components. For example, organic acids can react with iron, copper, and other materials in fuel systems to produce corrosion that can lead to the failure of fuel injectors, pumps, and other fuel-system components.
- Deposit formation within fuel injectors, on engine valves, or inside the combustion chamber. For example, trace metals can catalyze liquid-phase polymerization reactions that lead to the formation of lacquers, gums, and products that are insoluble in the fuel, which can foul close-tolerance fuel-injector components.
- Fuel-borne particulates that adversely affect fuel-injector operation. For example, if the fuel filter is not functioning properly, fuel-borne particles can plug small orifices in the fuel injector and/or lead to accelerated wear of injector components.
- Poisoning of exhaust-aftertreatment catalysts. For example, sulfur and phosphorus can cause active sites on catalytic aftertreatment devices to become temporarily or permanently inactive.
- Raising the cloud point and/or plugging the fuel filter with crystals. For example, high-melting-point impurities can be the first to freeze in colder climates, and their crystals can plug the fuel filter and thereby prevent the engine from running.
- Causing fuel blends to separate into two or more distinct liquid phases. For example, even small quantities of water can cause some fuel blends, especially those containing both polar and non-polar components (see Section 4.3.2), to separate.
- Decreasing autoignition delay time. For example, naturally formed peroxides can substantially decrease the autoignition-delay time of diesel fuels and gasolines.

Potential issues associated with trace components are discussed in more detail in the following section on key fuel properties.

Not all trace components in fuel are detrimental to performance. Cetane improvers, fuel stabilizers, lubricity improvers, metal deactivators, and detergents are examples of compounds that are routinely added to fuels at ppm (parts per million) levels to improve fuel performance in certain engine applications. The collection of these compounds used in a market fuel, called the "additive package," depends both on base-fuel characteristics and on the application.

3.4. Gaseous Fuels

Gaseous fuels face two primary challenges in transportation and other mobile-engine applications. The first is that they tend to be difficult to store at high energy density, often requiring high-pressure fuel tanks and/or cryogenic systems. The second is that they tend to lack a distribution infrastructure for transportation applications, i.e., there is no nationwide network of gaseous-fuel filling stations like there is for gasoline and diesel fuel. Nevertheless, gaseous fuels are an important piece of the puzzle of meeting global energy demand. The gaseous fuels of primary interest are natural gas and hydrogen.

3.4.1. Natural Gas

Natural gas is a mixture of hydrocarbons with carbon numbers typically in the range from one to four and existing in vapor form at standard conditions. The cetane number of natural gas is typically very low (< 0), its octane number is typically high (> 110), and its specific composition can vary widely depending on its geographical origin. The amount of recoverable natural gas in the world has dramatically increased in recent years due to the employment of hydraulic fracturing ("fracking") techniques for its production.

3.4.2. Hydrogen

There has been a great deal of interest in hydrogen because it does not contain carbon and hence its combustion does not produce the greenhouse gas CO_2. Nevertheless, the world currently lacks inexpensive and abundant sources of hydrogen, an established infrastructure for its distribution, and low-cost techniques for storing it at high energy density. Until these significant barriers are overcome, hydrogen is likely to remain a fuel of the future.

3.5. Fuel Mixtures

4. KEY FUEL PROPERTIES

From a high-level perspective, the processes occurring in modern internal-combustion engines are quite simple: oxygen from the air surrounding the engine is mixed with a fuel in a carefully controlled fashion, and both participate in combustion reactions that produce pressure and heat in the engine cylinder, plus major and minor product species. The pressure and heat created within each engine cylinder during combustion cause the engine pistons to move, and this movement transforms some fraction of the chemical energy from the fuel into the desired power at the crankshaft.

Air is composed of approximately 78 mol% molecular nitrogen (N_2) and 21 mol% molecular oxygen (O_2). When a liquid fuel composed of hydrogen, carbon, and perhaps some oxygen, nitrogen, and sulfur is burned in an engine, the vast majority of the atoms react to form the major product species CO_2 and H_2O. The CO_2 and H_2O pass out of the engine through the exhaust valves with N_2 from the intake air, perhaps some O_2 that was not consumed during the in-cylinder reactions (depending on the combustion strategy), and other minor product species including nitrogen oxides (NO_x), particulate matter (PM), carbon monoxide (CO), sulfur oxides (SO_x), and products of incomplete combustion (also known as unburned hydrocarbons or simply HC). The amounts of the minor species that leave the engine can depend strongly on fuel characteristics.

While the processes above are straightforward, the devil is in the details, and there are a great many mechanisms by which fuel properties can affect engine operation in subtle and not-so-subtle ways. In this regard, it is sometimes helpful to distinguish between fuel properties that are determined by the bulk fuel composition (e.g., density, aromatic content, distillation curve), versus those that can be significantly affected by trace levels (~1% or less) of certain compounds in the fuel (e.g., cetane number, lubricity, sulfur content). For instance, properties in the latter group sometimes can be improved through the use of fuel additives, while those in the former group cannot. It is also helpful to recognize that fuel properties are often inter-related (e.g., cetane number, density, and sooting propensity). As a result, it can be very challenging to determine the effects of changing a certain fuel property when other fuel properties necessarily change with the property of interest.

The objective of this section is to provide an overview of a number of key fuel properties and explain why they are important. The broad categories treated below are: combustion properties, physical properties, stability, materials compatibility, and environmental considerations.

4.1. Combustion Properties

The primary combustion properties of a reciprocating-engine fuel are its energy content, its autoignition quality, and its emissions-formation characteristics. These topics are treated in turn in the sub-sections below.

4.1.1. Energy Content

As mentioned in the Introduction, the energy content of a fuel, i.e., the amount of chemical energy available per unit mass (specific energy) or per unit volume (energy density), is a key factor in mobile-engine applications, because it plays the primary role in determining the mass and volume of fuel that must be carried aboard the vehicle or machine to satisfy the application requirements. Also, because fuels are typically sold by volume, energy density typically influences operating costs. One way to better understand the effects of fuel energy content is to consider the similarities and differences among the concepts of efficiency, fuel economy, and specific fuel consumption.

4.1.1.1. Efficiency, Fuel Economy, and Specific Fuel Consumption

Other chapters of this Encyclopedia cover engine and vehicle efficiency, fuel economy, and specific fuel consumption in greater detail, but certain aspects that are directly related to fuel effects bear mentioning here. For instance, an engine might run more efficiently when fueled with ethanol, but the corresponding fuel economy could be lower and the specific fuel consumption higher. How could this be? To answer this question, the definitions of efficiency, fuel economy, and specific fuel consumption must be considered within the context of variable fuel properties.

Efficiency, denoted η, is simply the engine work output per unit of chemical energy input, i.e.,

$$\eta = \frac{W_{out}}{m_f q_{LHV}}, \qquad (4.1)$$

where W_{out} is the work output per cycle of the engine, m_f is the mass of fuel supplied to the engine per cycle, and q_{LHV} is the lower heating value of the fuel (i.e., the specific energy of the fuel assuming the water in the products remains in the vapor phase). From a thermodynamic standpoint, an optimal engine design is one with maximum efficiency. Nevertheless, liquid fuels are priced on a volumetric basis rather than an energy-content basis, and hence the engine user often cares most about the fuel economy (FE) of the vehicle, i.e., the distance that can be traveled per unit volume of fuel. Since the distance that can be traveled is proportional to the work output of the engine, Eq. 4.1 can be used to show that

$$FE \propto \frac{W_{out}}{V_f} = \frac{\eta m_f q_{LHV}}{m_f / \rho_f} = \eta \rho_f q_{LHV}. \qquad (4.2)$$

In Eq. 4.2, V_f and ρ_f are the volume of fuel injected per cycle and the fuel density, respectively. So while the FE is proportional to the efficiency, as expected, it is also proportional to the fuel density and specific energy. Similarly, specific fuel consumption (SFC) is often used to quantify efficiency. SFC is the mass of fuel required per unit of work output, and again using Eq. 4.1,

$$SFC = \frac{m_f}{W_{out}} = \frac{1}{\eta q_{LHV}}. \qquad (4.3)$$

The presence of the specific-energy term in Eq. 4.3 indicates that, like FE, SFC is not a direct measure of efficiency. The subtle differences among η, FE, and SFC can be the source of considerable confusion.

Consider a gasoline-fueled vehicle with a FE of 40 miles per gallon (mpg) and an engine efficiency of 30%. Assuming that the same engine running on neat ethanol achieves an efficiency of 40%, a substantial thermodynamic improvement, the corresponding FE would only be 35.6 mpg. (This analysis assumes gasoline and ethanol specific energies of 42.6 and 27.0 MJ/kg, respectively; gasoline and ethanol densities of 749 and 789 kg/m^3, respectively; and all other vehicle parameters being equal.) The lower FE for neat ethanol is because even though the efficiency and density terms in Eq. 4.2 increase when switching from gasoline to neat ethanol, the specific energy of ethanol is low enough to counteract these effects. Hence, even with the increased engine efficiency of neat ethanol and if neat ethanol were available for 10% less cost per unit volume than gasoline, it would not make financial sense to switch from gasoline to neat ethanol based on the fuel cost per mile traveled. In this example, the lower specific energy of ethanol also leads to a higher SFC than that achieved with the gasoline-fueled vehicle. (Note: This is an example that was presented to illustrate some of the potential issues when considering the use of fuels with different energy contents; it is not a true cost/benefit comparison between gasoline and neat ethanol because the efficiency and FE values used were only hypothetical.)

As illustrated in the above example, efficiency is the best parameter to use when evaluating fuel effects on the ability of an engine to convert chemical energy into useful work, while FE is likely a better parameter to use for fuel-cost comparisons, and SFC might be desirable in situations that are very sensitive to the mass of fuel that must be carried aboard a vehicle.

4.1.2. Autoignition Quality

Autoignition quality is a critical characteristic of fuels for both SI and CI engines. In SI engines, autoignition quality is arguably the most important fuel property, determining the extent to which knock and pre-ignition phenomena will limit engine performance. Due to this critical role, fuel effects on SI engine knock and pre-ignition are treated in detail in the following subsection. Autoignition quality also plays an important role in CI engines, affecting cold-startability, combustion noise, and emissions, and these are discussed after the sub-section on SI-engine effects.

4.1.2.1. Fuel Autoignition-Quality Effects in SI Engines: Knock and Pre-Ignition

Knock in SI Engines

Knock is an abnormal combustion phenomenon that can damage spark-ignition (SI) engines [15] and is determined by the pressure and temperature history of the “end-gas” (i.e., the gas mixture ahead of the advancing flame front) and the anti-knock or autoignition quality of the fuel. Knock occurs when the end-gas autoignites, centered on one or more “hot spots,” causing a sharp rise in the heat release rate and setting up pressure waves in the cylinder which in turn manifest themselves as a metallic “pinging” sound. Knock intensity is usually defined as the maximum amplitude of this fluctuating pressure signal. When the knock intensity reaches some threshold value (it is common to use a value of 0.2 bar), the engine is said to knock.

At a given engine operating condition, knock intensity increases as the spark timing is advanced, and the timing at which the engine knocks is known as the Knock Limited Spark Advance (KLSA). The larger the KLSA, the more resistant a fuel is to knock at the particular operating condition. When the engine cannot be run at its maximum load and efficiency because of knock, it is said to be knock limited. A modern car includes a knock detector and is knock limited on normally available fuels over at least a part of its operating range. When knock is detected, the engine management system takes corrective action (e.g., it retards the spark timing), and this usually reduces the power. In such engines fuel anti-knock quality also can be quantified by measuring the knock-limited power or acceleration performance at a given operating condition [16,17]. Using a fuel with an anti-knock character higher than that required to avoid knock will not generally further improve engine performance, though use of a higher-octane fuel may improve fuel economy if the higher octane is achieved by a higher mole fraction of aromatic carbon in the fuel, since this type of fuel will have a greater energy density (see Section 4.1.1).

Fuel anti-knock quality is described by empirical measures because the fundamental autoignition chemistry cannot be quantified adequately for practical fuels due to their compositional complexity. It is traditionally measured by Research and Motor Octane Numbers, RON and MON, of the fuel used. The RON test is run in a single-cylinder Co-operative Fuel Research (CFR) engine at an engine speed of 600 rpm and an intake temperature of 52 °C, while the MON test is run at 900 rpm with a higher intake temperature of 149 °C. These tests are run in strict accordance with the procedures set in [18-20]. The octane scale is based on two alkanes, n-heptane (octane number ≡ 0) and iso-octane (octane number ≡ 100). The blends of these components are referred to as primary reference fuels (PRF) and define the intermediate points in the RON or MON scale. The RON or MON is the volume percent of iso-octane in the PRF. Thus a blend of 90 vol% iso-octane and 10 vol% n-heptane is assigned the octane number of 90 in both RON and MON scales. A fuel is assigned the RON (or MON) value of the PRF that matches its knock behavior in the RON (or MON) test. All practical gasolines are mixtures of aromatics, olefins, naphthenes, oxygenates, and alkanes. A practical gasoline will match the PRF of a higher octane number in the RON test and hence has a higher RON when compared to the MON test. The difference between RON and MON is known as the sensitivity.

Pressure and temperature development in the unburned gas in an engine

The temperature of the unburned gas increases as pressure increases in the engine cylinder. For instance, at the RON test condition, the temperature at a given pressure is lower than in the MON test condition as shown in Fig. 4.1 [16]. Modern engines are "beyond RON" because the temperature of the unburned mixture, at a given pressure, is even lower than in the RON test. Alternatively, the pressure for given temperature is higher in modern engines compared to the RON test. An example of such a condition "beyond RON" is also shown in Fig. 4.1. This is a consequence of the higher efficiency of modern engines. Engine designers have always tried to force more air into the cylinder while minimizing the temperature in order to improve power density and efficiency. Indeed, all the modern trends aimed at improving the efficiency of SI engines such as increasing the compression ratio, direct injection and turbo-charging aligned with down-sizing will push modern engines further "beyond RON."

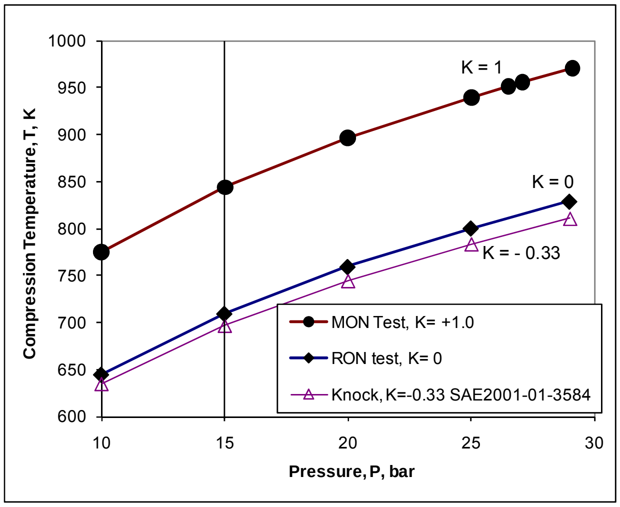


Figure 4.1. Unburned mixture temperature vs. pressure. K decreases from 1 to zero moving from the MON test condition to the RON test condition and becomes negative "beyond RON." The true anti-knock quality is given by OI = (1-K)RON + K*MON.

Anti-knock quality of gasolines in modern engines

The anti-knock quality of a fuel varies with engine conditions. Thus the knocking characteristics of a gasoline of 95 RON and 85 MON will match those of an 85 PRF in the MON test, while it will be much less prone to knock, compared to PRF fuels, in the RON test condition and will match 95 PRF. This is because the autoignition chemistry of non-alkane components in gasoline is different from that of PRF. The anti-knock quality of practical fuels in an engine is studied by measuring a parameter dependent on the autoignition quality of the fuel such as KLSA. At the same operating condition many fuels of different chemical compositions and hence, different RON and MON, are compared. In such autoignition studies, Homogeneous Charge Compression Ignition (HCCI) engines have been valuable complements to knocking SI engines because the fundamental combustion mechanisms are the same in both cases, as summarized in [16]. However, it is possible to run HCCI engines well "beyond RON" or even well "beyond MON" by increasing the intake pressure or intake temperature. This has allowed autoignition behavior to be studied in pressure/temperature regimes not accessible in knocking SI engines.

The true anti-knock quality of a gasoline is best described by an Octane Index, OI [16,17] which is defined as

$$OI = (1-K)RON + K*MON = RON - K*S \qquad (4.4).$$

where K is an empirical constant which depends only on the pressure and temperature history of the unburned mixture in the cylinder and S = (RON – MON) is the sensitivity. OI is the octane number of the PRF that matches the knock behavior of the gasoline that is of interest, at the conditions of the particular engine test. The value of K depends on the design and operating condition of the engine. Thus K=1 in the MON test and the anti-knock quality of the gasoline is described by its MON but K=0 in the RON test which runs at a lower temperature for a given pressure (Fig. 4.1). Modern engines are "beyond RON" and K is negative, i.e. for a given RON, a lower MON, higher sensitivity fuel has higher OI and is more resistant to knock. For instance, if K = -0.5, a gasoline with 95 RON and 85 MON will have an OI of 100 and will actually match a PRF of 100 (i.e., pure iso-octane) for knock. Modern engines usually have negative K values [16,17,21-23].

The value of K has been decreasing throughout recent history

The RON test was invented in 1930 when the average compression ratio was around five [24], and the engines had poor efficiency compared to modern engines. It was soon obvious that the RON test did not predict the anti-knock quality of fuels on the road at that time. Hence the MON test was developed and it reflected the anti-knock behavior of fuels in cars of that time much better. Clearly, the K value of the U.S. car fleet then was around 1. The Coordinating Research Council (CRC) in the U.S. has conducted frequent surveys to establish the octane appetite of U.S. cars between 1947 and 1996. Based on these data and other available sources, Mittal and Heywood [24] show that the K value has decreased from around 1 to zero in 2008 because of reduced end-gas temperatures and higher pressures. A similar decreasing trend for K in the U.K. car fleet also has been reported in [16]. Historically in the U.S., fuel anti-knock quality has been assumed to be best described by (RON+MON)/2, which translates into K = 0.5. The U.S. car fleet, on average, used to have such an octane appetite when this specification was first agreed upon; however, engine technology has moved on and with it, the octane appetite.

Why is K negative in modern engines?

The autoignition chemistry of non-alkane components which are found in practical fuels is significantly different from that of the PRFs used in the RON and MON scales. In general, for a given temperature, T, a non-alkane fuel becomes more resistant to autoignition, compared to an alkane fuel, as the pressure, P, increases. A fundamental measure of autoignition quality of a combustible mixture is the ignition delay, τ, which is measured outside the engine in special equipment such as shock tubes or rapid compression machines [15,25,26]. The smaller the value of τ, the more reactive is the mixture. In general, τ can be expressed as a function of temperature and pressure [25,26] in a given pressure/temperature range.

$$\tau = \tau_0 f\left[(T/T_0)(P/P_0)^{-n}\right] \qquad (4.5)$$

Here τ_0 is the ignition delay measured at some reference pressure, P_0, and a reference temperature, T_0. It is found experimentally that the value of the pressure exponent, n, is much smaller for non-alkane fuels compared to alkane fuels [25,26] at high temperatures ($T > \sim 850$ K). Hence, non-alkane fuels become relatively more resistant to autoignition if the pressure is increased at a fixed temperature. Why this should be so, at the fundamental chemical kinetic level, is not yet clear. The negative value of K could only be explained in HCCI engines [27] and in knocking SI engines [17] by this difference in the value of the pressure exponent, n, between alkane and non-alkane fuels. The sensitivity, S, is a measure of how different the fuel autoignition chemistry is from that of PRF.

Specifications for fuel anti-knock quality and engine appetites

High MON is considered to contribute to the anti-knock quality of a gasoline in many areas, e.g., in North America and in Europe. In Europe, there is a minimum MON specification of 85 and in North America MON is considered to be as important as RON. However, as discussed above, modern engines have pressure/temperature development regimes which make MON at best irrelevant ($K = 0$) or actually detrimental to fuel anti-knock quality ($K < 0$). Thus these octane specifications are inconsistent with the actual requirements of modern engines. Moreover, as improved engine efficiency is sought, this mismatch between specifications and engine requirements will get wider and will have to be addressed. Steps taken to improve engine efficiency such as down-sizing and turbo-charging will in general make future engines more prone to knock, necessitating higher anti-knock quality in the fuel. Such engines will also be "beyond RON," and the K value will be negative so that for a given RON, a lower-MON fuel will be more resistant to knock [28]. The need to bring fuel specifications in line with engine requirements will increase.

Pre-ignition and "Superknock"

Pre-ignition is an abnormal combustion phenomenon where an expanding flame front is established before the spark plug fires in the engine. Pre-ignition has been of intermittent concern at different stages of the history of SI engines. In the 1950s and early 1960s, compression ratios increased rapidly and pre-ignition became a serious problem. Pre-ignition again seems to have attracted attention in the 1980s primarily because of the problems encountered with using methanol after a relatively quiet period in the 1960s and 1970s. With the trend in down-sizing and turbocharging, it has again become a concern in turbo-charged DISI (Direct Injection Spark Ignition) engines [29,30]. The early start of combustion from pre-ignition causes the pressure and the temperature of the unburned gas ahead of the advancing flame front, the end-gas, to rise more rapidly compared to normal spark timing. If autoignition occurs in the end-gas at high pressure and temperature, it can lead to extremely heavy knock, with knock intensities of 100 bar or more. Such events are informally described as "super-knock," another abnormal combustion phenomenon which could potentially damage the engine [30,31].

Pre-ignition is a flame initiation problem and two separate criteria have to be met in order for it to occur. The first is an ignition criterion which requires that the temperature must reach a minimum level locally so that runaway chemical reactions start. This might occur because of hot spots on the internal surfaces of the engine or because of autoignition and catalytic reactions centered around oil droplets or particulates in modern DISI engines. The additional initiation criterion requires that the incipient flame must reach a critical radius which is proportional to the laminar flame thickness, δ, before it becomes self-sustaining [31]. The smaller the value of δ, the larger is the probability of flame initiation and pre-ignition, all else being equal. In the experiments reported in modern DISI engines [29,32], the probability of both criteria being satisfied is low since pre-ignition only occurs every 15,000 cycles or so. However, all else being equal, anything that reduces δ will make pre-ignition more likely.

Assuming the Prandtl number to be unity, δ can be related to the dynamic viscosity, μ, the density, ρ, and the laminar burning velocity S_l, by [31]

$$\delta = (\mu / \rho S_l) \tag{4.6}$$

Further, S_l is related to the pressure, P, and temperature, T, by

$$S_l = S_{l0}\,(T/T_0)^n (P/P_0)^{-m} \tag{4.7}$$

where S_{l0} is the laminar burning velocity at some reference pressure, P_0, and temperature, T_0 and m and n are constants [33,34]. Also, from the ideal gas law, $(P/P_0) = (T/T_0)(\rho/\rho_0)$ where ρ_0 is the density at pressure P_0 and temperature T_0. Finally dynamic viscosity, μ, varies as $T^{0.5}$. If μ_0 is the dynamic viscosity at P_0 and T_0, from Eq. 4.6,

$$\delta = \left(\frac{\mu_0}{\rho_0 S_{1,0}}\right)\left(\frac{P}{P_0}\right)^{m-1}\left(\frac{T}{T_0}\right)^{1.5-n} \tag{4.8}$$

As pressure is increased in an engine, the temperature also increases so that $T/T_o = (P/P_o)^{(x-1)/x}$ where x is the polytropic index. Taking $x = 1.35$, $T/T_o = (P/P_o)^{0.26}$. Hence Eq. 4.8 can be rewritten as

$$\delta = \left(\frac{\mu_0}{\rho_0 S_{1,0}}\right)\left(\frac{P}{P_0}\right)^{m-0.26n-0.61} \tag{4.9}$$

The kinematic viscosity, μ_0 / ρ_0, of the fuel/air mixture for different liquid fuels can be assumed to be the same. The values of *m* have been reported to be between 0.16 and 0.28, whereas n is between 1 and 2.2 for different fuels [31]. Hence, for a given fuel (i.e., with S_{l0} fixed), the pressure exponent in Eq. 4.9 is always negative so that as pressure increases, the laminar flame thickness decreases and pre-ignition becomes more likely. Experimentally, for a given fuel, pre-ignition is also found to be more likely if the mixture strength is slightly rich of stoichiometric, where S_{l0} is likely to be maximum [35]. We should also expect that for a given fuel, use of cooled EGR will reduce S_{l0} and hence make pre-ignition less likely, all else being equal. For a given operating condition as we test different fuels, we should expect that as S_{l0} increases, pre-ignition becomes more likely and pre-ignition resistance (*PR*) decreases. This is indeed found to be the case [31]. Figure 4.2 shows *PR* from [35] for different fuels plotted against the maximum laminar burning velocity, S_{lmax} measured at 30.4 bar (P_0) and 450 K (T_0) in [36]. *PR* in [35] was measured at a mixture strength slightly rich of stoichiometric where the laminar burning velocity is likely to be maximum. There was little correlation between *PR* and RON or PR and MON, confirming what has been found in all previous studies [31].

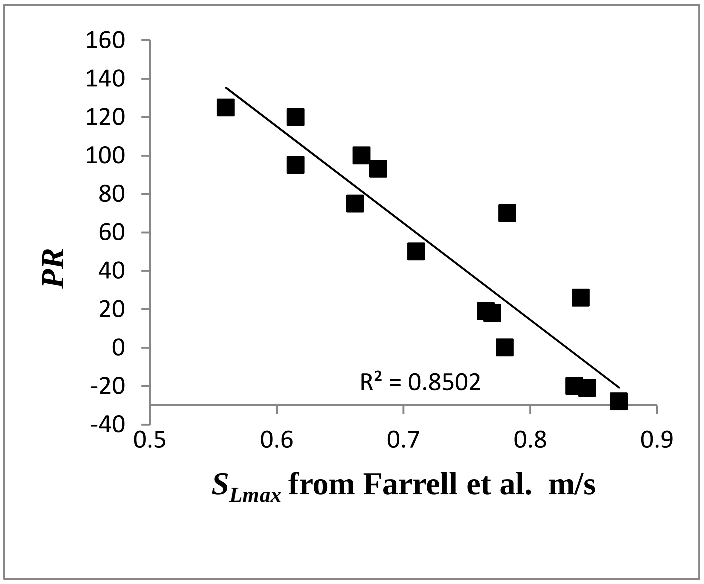


Figure 4.2. Pre-ignition resistance (*PR*) from [35] vs. S_{lmax} from [36].

Pre-ignition increases pressure and temperature in the end-gas ahead of the advancing flame front. The mixture in the end-gas is never homogeneous and the autoignition that triggers knock is initiated at one or more centers or “hot spots.” The pressure wave initiated by the autoignition changes as it traverses through inhomogeneities in the end-gas [37]. Similar phenomena also occur in homogeneous charge compression ignition (HCCI) engines [38]. Hot spots are associated with gradients of reactivity which lead to gradients of autoignition-delay time. The pressure wave generated by the hot spot can couple with the autoignition reaction front when it moves into the unburned mixture at approximately the acoustic speed. Under some circumstances, the fronts are mutually reinforced to create a damaging pressure spike propagating at high velocity within the hot spot in a *developing detonation* [39]. If autoignition occurs at these high pressures and temperatures, the probability of developing detonation increases and this is the most likely explanation for the extremely high intensity knock, informally known as "super-knock," that is occasionally observed in modern turbo-charged DISI engines following pre-ignition [30,31].

4.1.2.2. Fuel Autoignition-Quality Effects in CI Engines

In most modern CI engines, the majority of the fuel is injected directly into the combustion chamber when the piston is near the top of the compression stroke. Within a given time after the start of injection (SOI, i.e., the time at which fuel begins to enter the combustion chamber), fuel-rich regions of the stratified mixture in the cylinder autoignite, creating a rapid pressure increase. The rest of the fuel burns in a quasi-steady lifted jet diffusion flame [40]. The time between SOI and autoignition is called the ignition delay. In general, a given change in ignition-delay time will have a larger effect in a high-speed engine than a low-speed engine because the crankshaft rotates through a larger angle per unit time in the high-speed engine.

The autoignition quality of fuels for CI engines is typically quantified using the cetane number (CN). In general, fuels with short ignition delays have higher CNs, and fuels with longer ignition delays have lower CNs. Typical diesel fuels have cetane numbers between 40 and 60. High-CN fuels are preferable for use in conventional CI engines. Their tendency to autoignite easily facilitates engine cold-starting. High-CN fuels also lead to quieter engine operation. The shorter time for fuel-air premixing during the ignition delay for high-CN fuels leads to a smaller amount of chemical energy release during premixed autoignition, and hence quieter combustion (all else being equal).

The CN of a fuel is measured using an indirect-injection single-cylinder CFR (Co-operative Fuel Research) engine with a pintle-type fuel injector and an adjustable compression ratio operated at a constant speed of 900 rpm, as described in ASTM International Test Method D613 [41]. The conditions used in the cetane-engine test are not very representative of those in modern CI engines. Other test methods employing constant-volume combustion chambers to measure the Derived Cetane Number (DCN) also are becoming more widely used [42,43], but their results are based on correlations with cetane-engine data, so they are no more representative of conditions in modern engines.

While the ignition delay is a function of the conditions within the engine cylinder (e.g., temperature, pressure, local mixture stoichiometry), it is also a function of the fuel-composition-dependent chemistry that occurs as the fuel begins to oxidize. The autoignition quality of a low-CN base fuel can be improved without changing the bulk fuel composition by adding tens to hundreds of ppm of a highly reactive "cetane improver" to the fuel. The most common cetane improvers in use today are 2-ethylhexyl nitrate (EHN) and di-tert-butyl peroxide (DTBP). The effects of EHN addition on diesel-fuel CN are discussed in [44].

A treatment of the detailed processes leading from possible low-temperature (or "cool-flame") reactions through high-temperature ignition is beyond the scope of this article, but this area has been well addressed in the literature [45-48]. Suffice it to say that kinetic effects on autoignition processes can be complex. Alkanes, aromatics, and oxygenates can and do exhibit markedly different behaviors under certain conditions. As mentioned in the preceding section, the need for new autoignition-quality metrics to better characterize the ignition behaviors of modern fuels in modern engines has been acknowledged, but such new metrics have not yet found their way into widespread use.

4.1.3. Emissions-Formation Characteristics

It is often easy to observe that changing the composition of the fuel supplied to an engine can change the emissions characteristics of the engine. Less straightforward, however, is understanding the mechanisms underlying the observed emissions changes. This is because fuel-composition changes can influence physical, chemical, and engine-calibration-specific processes. (The engine calibration establishes the exact values of the various input parameters required for optimal operation at each point in the engine operating space.) Of these, engine-calibration-specific processes can be particularly difficult to understand because calibrations are usually proprietary in nature, costly to create, and not created for anything other than an average market fuel.

Examples of physical processes that can be affected by fuel-composition changes include:

- Fuel injection (e.g., injection pressure, timing, in-nozzle cavitation)
- Fuel vaporization (e.g., liquid- and vapor-phase fuel penetration, entrainment rate, droplet characteristics)
- Mixture formation (e.g., degree of fuel and thermal stratification, spray-wall interactions, presence of liquid-fuel films)

Examples of chemical processes that can be affected by fuel-composition changes include:

- Fuel autoignition resistance (and dependence on in-cylinder thermal and mixture stratification and pressure)
- Combustion kinetics (e.g., heat-release rate, emissions formation and removal, combustion stability)
- Mixture stoichiometry (i.e., the proximity of the charge-gas mixture at each point in space to its stoichiometric condition; see [49])
- Aftertreatment-system reactions and efficiency

Examples of fuel-dependent, engine-calibration-specific processes include:

- Injection/ignition timing changes
- Turbocharger settings changes
- Exhaust-gas recirculation rate changes
- Intake-manifold pressure and temperature changes
- Differences in any of the above between steady-state and transient conditions for different fuels

Based on the above, it should be expected that the magnitudes and even the directions of emissions changes will vary with fuel changes depending on: which fuel properties are varied (it is almost always impossible to vary only one fuel property at a time); how fuel properties are varied (e.g., if the aromatic content of a fuel is decreased, what kinds of compounds are replacing the aromatics?); the ranges over which fuel properties are varied (the effects of raising CN from 30 to 40 are likely to be larger than the effects of raising CN from 70 to 80); the specific engine and combustion strategy (fuel effects observed in a light-duty SI premixed-combustion mode are likely to be different from those observed in a heavy-duty CI mixing-controlled-combustion mode); the specific operating condition(s) and/or test cycle(s) employed (e.g., high- vs. low-load conditions, steady-state vs. transient cycle); and the presence, absence, nature, and/or age of any installed aftertreatment devices.

The use of biodiesel in CI engines provides an illustrative example of how changing the fuel can have a number of inter-related, subtle, and complex effects on engine-out emissions. First, biodiesel has a lower volatility than conventional diesel fuel, which can lead to longer penetration of liquid-phase fuel within the combustion chamber and subsequent wall impingement [50]. Wall impingement can lead to lower efficiency, reduced durability (due to loss of wear resistance when lubricant is diluted with fuel), and the formation of pool fires that can produce elevated emissions of smoke, NO_x, HC, and CO [51,52]. Second, the oxygen bound within biodiesel methyl esters pushes the fuel-rich autoigniting mixtures closer to stoichiometric conditions, leading to higher local temperatures that are further elevated by less radiative heat loss from the flame due to the lower levels of soot produced [53]. The higher temperatures lead to faster combustion reactions, producing an effective phasing advance. The higher temperatures and longer residence times at high temperature for biodiesel lead to increased thermal NO_x formation relative to a hydrocarbon diesel fuel [53]. Third, the lower energy content of biodiesel means that a larger quantity must be injected to achieve a given load. An engine calibrated for diesel fuel could interpret the larger quantity of fuel injected as a signal to reduce the EGR level, further increasing the NO_x emissions when fueling with biodiesel [54]. In principle, many of these factors can be overcome by re-calibrating the engine for biodiesel use, resulting in lower smoke, HC, and CO emissions at equivalent NO_x and efficiency levels relative to hydrocarbon diesel fuel [55]. There are costs and challenges involved, however, with recalibrating existing engines, as well as adjusting for different biodiesel blend levels (e.g., B5 vs. B100) and differences in biodiesels made from different feedstocks (e.g., soy vs. palm).

Trends in mixture-stoichiometry and temperature effects on emissions from both CI and SI engines can be estimated using a ϕ-T plot, as shown in Fig. 4.3 (from [56]). Soot production occurs in regions with $\phi > 2$, and the width of the temperature window over which it occurs increases with ϕ. NO_x production occurs in near-stoichiometric to lean mixtures with $T > 1900$ K. HC production occurs in mixtures with $T < 1000$ K and/or higher-temperature mixtures with $\phi > 1.2$. CO production occurs mostly in rich, high-temperature mixtures, though it can also occur in leaner mixtures where temperatures are insufficient to carry CO oxidation to completion. If the fuel is oxygenated, the oxygen equivalence ratio should be used in place of the conventional equivalence ratio to quantify the mixture stoichiometry [49].

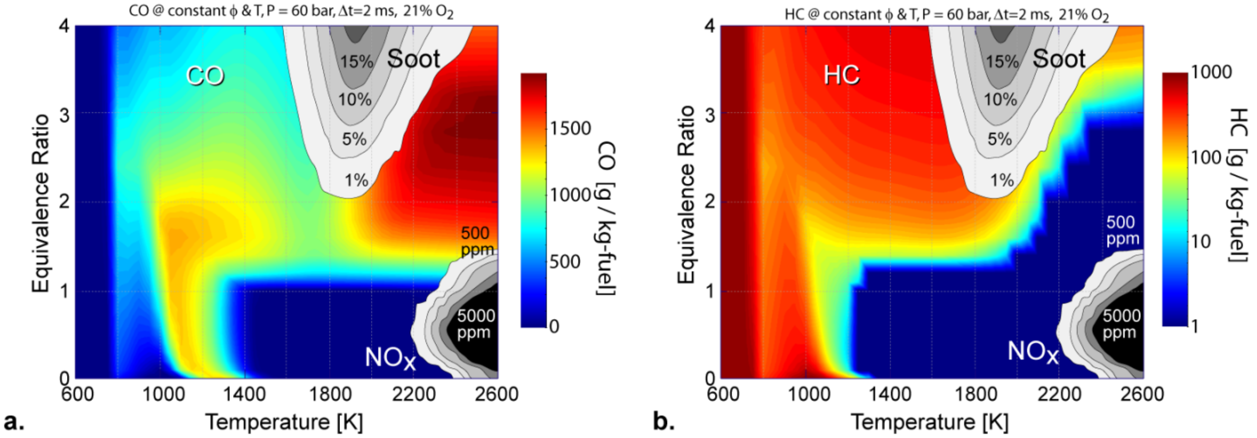


Figure 4.3. Emissions calculated in a constant temperature and pressure homogeneous reactor at a reaction time of 2.0 ms for n-heptane/air mixtures (i.e., no dilution) at the given local equivalence ratio and temperature. Contours indicate emissions indices of soot and NO_x [57], whereas colors indicate emissions indices of **a**. CO and **b**. HC [56].

Emissions trends also can change with fuel composition. Fundamental studies have shown that sooting tendency generally goes as: poly-aromatics > mono-aromatics > cyclo-alkanes > iso-alkanes > n-alkanes [58,59]. Fuel effects on NO_x emissions tend to be small, provided comparisons are made at the same mixture stoichiometry [60], though there is some evidence that NO_x emissions increase with aromatics content [61,62]. Trends for HC and CO emissions tend to be similar to one another. Lower emissions of these pollutants tend to be correlated with higher levels of more-reactive species (e.g., n-alkanes [63]). Other review articles that may be of interest regarding fuel effects on CI and SI engine emissions include [64] and [65]. A good review of fuel effects on 1998 and earlier heavy-duty CI engines can be found in [66].

4.1.4. Flash Point and Flammability Limits

The flash point is a parameter used to quantify the tendency of a fuel to form an explosive mixture, and it is often used to help assess potential safety issues related to fuel storage and handling. The flash point is the temperature at and above which the vapors over a layer of liquid fuel will sustain a flame if an ignition source is provided. Many methods exist to measure the flash point, and the values yielded by different methods for a given fuel will not necessarily be equal. Nevertheless, the flash point is the most widely used fire-safety parameter used in commercial practice.

Another way to assess the risk of fire or explosion resulting from an accidental fuel release is to measure the flammability limits of the fuel. Most gasoline- and diesel-range hydrocarbons will sustain combustion only in a narrow range from ~1 – 7 vol% in air at standard conditions. Fuel-storage systems are designed so the mixture in the fuel tank remains above the rich flammability limit for gasoline-fueled vehicles and below the lean flammability limit for diesel-fueled vehicles over a wide range of ambient conditions. While the lean flammability limits for methane and hydrogen are slightly higher than those of gasoline- and diesel-range hydrocarbons at 5 and 4 vol%, respectively, the rich limits are significantly higher at 15 and 74 vol%, respectively. This phenomenon and the high tank pressures often associated with methane- and hydrogen-fueled vehicles require that special safety precautions be taken to protect against fire and explosion in the event of an accidental release when these gaseous fuels are employed.

4.2. Physical Properties

4.2.1. Phase-Change Characteristics

A fuel must satisfy a few primary phase-change requirements to perform well in a given reciprocating-engine application. First, the fuel must generally be a liquid when it is pumped to the injectors. Solid and vapor-phase fuels are not compatible with conventional liquid-fuel pumps, and will generally lead to filter plugging and "vapor lock" (loss of fuel pressure due to vaporization in the fuel-supply system), respectively. Second, any fuel must be vaporized before it can be burned in the combustion chamber. Liquids and solids cannot burn in the conventional sense; some of the condensed phase must be converted to vapor and mixed with a sufficient amount of oxygen before combustion can occur. Third, the fuel should not be so volatile that a significant fraction of it is lost from the tank and/or fuel-transfer lines over time (these evaporative emissions can adversely impact air quality), but it should be volatile enough that the engine starts easily under cold conditions. Most fuel specifications related to phase-change characteristics exist to ensure that these three requirements are met.

4.2.1.1. Maintaining Liquid-Phase Fuel in the Fuel-Supply/Injection System

Ensuring that the fuel remains in the liquid phase within the fuel system imposes different challenges depending on fuel type, composition, climate at a given geographical location and time of year, altitude, and engine application. For gasolines, the challenges typically occur due to excessive liquid-to-vapor transition. Gasoline volatilities have been limited to prevent vapor lock in hot weather [67]. The vaporization characteristics of a fuel are typically quantified by measuring its distillation curve. The distillation curve is typically quantified using the ASTM D86 test method [68], though alternative methods with an improved grounding in thermodynamics have been proposed [69]. For diesel fuels, the challenges associated with phase change typically occur due to undesired liquid-to-solid transition. Fuel freezing or gelling can cause fuel filters to plug, thereby stopping the engine. A number of test methods have been designed to quantify the potential cold-weather issues with diesel fuels, including the cloud point [70], pour point [71], cold filter plugging point [72], and the low-temperature flow test [73].

4.2.1.2. Achieving Desired Fuel Vaporization in the Engine

The lower volatilities of diesel fuels also can present problems with in-cylinder vaporization, which can lead to lower efficiencies and higher emissions, especially when advanced or retarded injection timings cause the fuel to be injected into a cooler in-cylinder environment [50-52]. The main parameter affecting adequate gasoline vaporization is the back-end volatility (i.e., the high-temperature end of the distillation curve). Oxygenate addition can also introduce challenges; for example, blending ethanol into gasoline results in increased latent and specific heats and hence more energy required to vaporize the fuel.

4.2.1.3. Preventing Excessive Evaporative Emissions while Maintaining Cold-Start Performance

Evaporative emissions are primarily an issue with gasolines, and they are governed by the vapor pressure of the gasoline. The vapor pressure should be as low as possible to minimize evaporative emissions, while still being high enough for the fuel to deliver adequate performance under cold-start conditions. Vapor pressure can be quantified using a number of different test methods; see [67] for a list. Oxygenate addition can also introduce challenges with vapor pressure. For example, blending ethanol into gasoline results in an increased vapor pressure of the blend. Excessive vaporization is not typically a problem with diesel fuels due to their lower volatilities; the notable exception is if gasoline has been blended into diesel fuel.

4.2.2. Density

Density is a fundamental physical property of a fuel, and it can influence fuel utilization through a number of mechanisms. As discussed in Section 4.1.1.1, the density of a fuel can affect fuel economy and fuel consumption. Fuel density changes also can affect the penetration of liquid and vapor-phase fuel within the combustion chamber, as well as the engine calibration. Aromatic hydrocarbons and oxygenates generally have higher densities than aliphatic hydrocarbons of the same carbon number.

4.2.3. Lubricity

The lubricity of a fuel is its ability to prevent the wearing of adjacent wetted parts that move relative to one another. Fuel lubricity is an important parameter, particularly in CI-engine applications where the fuel pump and injectors are lubricated by the fuel, include close-tolerance parts, and may operate at pressures exceeding 250 MPa. The lubricity of a fuel is the combination of its hydrodynamic- and boundary-lubrication characteristics. Hydrodynamic lubrication is provided by the fuel viscosity preventing adjacent parts from touching (higher viscosities are better), while boundary lubrication is provided by the fuel adhering (via intermolecular forces) to the adjacent solid surfaces [5]. Fuel lubricity can be quantified using a number of test methods, with the high-frequency reciprocating rig (HFRR) [74] and scuffing load ball on cylinder lubricity evaluator (SLBOCLE) [75] being the most common in the US. Lubricity is a property that can be significantly improved by fuel additives blended at treat rates significantly less than 1 wt%.

4.2.4. Viscosity

The viscosity of a fuel affects its hydrodynamic lubrication characteristics, as discussed above. Viscosity also influences fuel pumping and atomization. A fuel with low viscosity will tend to leak through small clearances in a fuel pump, which may lead to reduced delivery pressures and quantities. Lower viscosity (and lower surface tension) have been shown to enhance liquid-fuel atomization, but this mechanism may be less important for the injection pressures and ambient conditions in modern CI engines [76,77].

4.2.5. Electrical Conductivity

A static charge can accumulate when a fuel is being pumped from one location to another. In the absence of proper grounding, the potential difference between a given fuel-system component and ground can become large enough for a spark discharge to occur. This spark could act as an ignition source for fuel vapors, and a fire or explosion could ensue. Conductivity-enhancing additives are used when necessary to mitigate this potential hazard.

4.3. Stability

The stability of a fuel refers to its resistance to changes in its chemical composition and/or mixture characteristics over time. A fuel with excellent stability is desirable. There are two main types of fuel instability: chemical instability and mixture instability.

4.3.1. Chemical Instability and Deposit Formation

A fuel that undergoes oxidation, polymerization, or other reactions in the liquid phase that change its composition has chemical instability. The chemical reactions of oxidation or polymerization can produce generally higher molecular-weight compounds that are insoluble in the fuel, such as lacquers, gums, and solids. These species are called deposits if they adhere to fuel-system, in-cylinder, or other engine components. Such deposits can plug fuel filters, prevent proper injector operation, foul in-cylinder components like piston rings and valves, and increase engine emissions. For example, the relatively lower oxidative stability of biodiesel relative to conventional hydrocarbon diesel fuel can lead to fuel-system deposits, which is why a number of engine manufacturers only warranty their systems for fuels with up to 5 vol% biodiesel content. In-cylinder deposits in SI engines are formed by various mechanisms and can be correlated with lower volatility and higher aromatic content of the fuel. They can lead to increased knocking which the knock sensor on modern engines will detect, causing the spark timing to be retarded and resulting in poorer acceleration performance, and to some extent, higher fuel consumption. Anti-oxidant additives are formulated to prevent the reactions leading to chemical instability, and detergent additives are formulated to control and, at higher concentrations, remove engine deposits after they have formed in the engine.

4.3.2. Mixture Instability and the Importance of Polarity

The second type of fuel instability is mixture instability. A fuel mixture is unstable if it separates into two or more distinct liquid phases over time, when exposed to different temperatures, or with the addition of a trace contaminant. All common fuels for reciprocating internal-combustion engines are mixtures. These mixtures contain compounds comprised of covalently bonded atoms. Some of these compounds have large permanent electrostatic-dipole moments (i.e., they have a net positive charge in one area of the molecule and a net negative charge in another), some do not, and still others will take on a dipole moment in the presence of an imposed electric field. The magnitude of the permanent or induced electrostatic-dipole moment of a compound is called its polarity. The polarities of different molecules have a strong impact on the types of mixtures they form and the stabilities of those mixtures.

Compounds with permanent electrostatic dipole moments are called “polar.” A high degree of polarity can be caused by the presence of one or more constituent atoms having different electronegativities. For example, the high electronegativity of oxygen tends to make oxygenated compounds polar. The attractive electrostatic forces between the positive and negative areas of polar molecules tend to hold polar molecules together, making their mixtures true solutions. For example, water and ethanol – both polar compounds – are miscible, i.e., they are soluble in all proportions.

Compounds that exhibit small permanent electrostatic dipole moments are called “non-polar.” Hydrocarbons are generally non-polar because the electronegativities of carbon and hydrogen are similar. Hydrocarbons readily form stable solutions with other hydrocarbons. When non-polar and polar molecules are combined, however, the attractive forces between polar molecules tend to keep them together rather than allowing them to mix with the non-polar compounds, hence the adage, “oil and water don’t mix.” The two types of compounds can be forced to mix through mechanical means (e.g., by putting them in a blender), producing an emulsion. An emulsion is essentially a suspension of droplets of high polarity in a distributed phase of low polarity, or vice versa. In general, buoyancy-driven stratification due to the different densities of the polar and non-polar fractions, coupled with a finite rate of coalescence of droplets of similar polarity, will cause the polar (or “hydrophilic”) compounds in an emulsion eventually to separate from the non-polar (or “hydrophobic”) compounds, unless other compounds are added to stabilize the mixture.

Finally, some hydrocarbons, while non-polar, are “polarizable.” The non-localized electron distributions of such compounds can allow them to take on an induced dipole moment due to the presence of polar molecules in the vicinity. Aromatic hydrocarbons are a classic example of polarizable compounds. Hence, ethanol is effectively insoluble in n-hexadecane, a largely non-polar and unpolarizable compound, but it is quite soluble in gasoline, especially gasoline that contains a large concentration of polarizable aromatic hydrocarbons.

Solutions generally will not separate over time, i.e., they exhibit mixture stability. Nevertheless, solubility typically depends on factors such as temperature, solute concentration, and the presence of trace species. For example, the addition of a small amount of water to an oxygenate-hydrocarbon mixture near its solubility limit also can cause the mixture to separate into two or more distinct liquid phases [78].

4.4. Materials Compatibility

Fuels come into contact with many materials as they move from their points of production through the engines they power, including materials in supertankers, pipelines, underground storage tanks, tanker trucks, dispensing pumps and lines, vehicle fuel tanks, fuel-level sensors, fuel-injection systems, engine components (valves, pistons, cylinder liners), lubricants, and aftertreatment devices. The materials in these systems have been carefully selected and optimized over decades of experience. New fuel blendstocks can lead to incompatibilities with existing infrastructure that can be expensive to rectify.

4.4.1. Corrosivity

One of the most important materials-compatibility properties of a fuel is its corrosivity. A fuel is said to be corrosive to a given metal if it chemically reacts with and degrades the surface quality of the metal over time at conditions experienced under normal system operation. Imagine the expense of repairing a pipeline corroded by flowing an incompatible fuel, or the cost of replacing corroded fuel injectors in tens of thousands of vehicles. Fuels that contain organic or inorganic acids or highly polar compounds such as water or methanol often are corrosive. Fuel corrosivity is commonly quantified using a test method in which a polished strip of copper is submerged in the fuel at an elevated temperature for several hours and then visually compared to reference strips [79]. Copper is used because it corrodes similarly to, but more quickly than ferrous metals. Sometimes a silver strip is used in place of copper because many fuel-level sensors contain silver [67].

4.4.2. Elastomer Compatibility

Another important factor to consider with new fuels is their compatibility with common fuel-system elastomers (i.e., the o-rings, gaskets, and hoses used in fuel injectors, pumps, and lines). Elastomers can swell, shrink, harden, soften, split, and even dissolve when exposed to different fuels. For example, nitrile-rubber elastomers used in conventional-hydrocarbon fuel-delivery systems swell when wetted by fuels that contain aromatics, and this swell is factored into the system designs. If these systems are used with low-aromatics fuels like F-T diesel or hydrotreated vegetable oil, the seals will not swell adequately, leading to potential fuel-system leakage and corresponding safety hazards. Oxygenates (e.g., ethanol and biodiesel) can present elastomer-compatibility issues as well. While elastomers that are compatible with a wider range of fuels do exist (e.g., perfluoroelastomers), they tend to be both more expensive than conventional-rubber elastomers and costly to replace on existing vehicles.

4.4.3. Catalyst Deactivation

The third primary materials-compatibility consideration with fuels has to do with the deactivation of the catalytic aftertreatment systems used to lower the emissions levels of regulated pollutants from most modern powertrains. Catalyst deactivation is a rich area of study, depending on the type of catalyst and the deactivation mechanism: chemical, fouling, thermal, or mechanical. Fuel properties most directly affect the first two of these mechanisms. Fuels that contain sulfur or phosphorus can "poison" a catalyst (i.e., lower its activity) by bonding or adsorbing to its active sites. Indeed, a key factor in the continual lowering of diesel-fuel sulfur levels in the US (to 15 ppm by weight currently for on-road engines) is to enable the use of sulfur-sensitive catalytic aftertreatment systems. Another fuel-dependent mechanism for catalyst deactivation is the physical blocking of active sites by fouling. The fouling agent could be soot, which can be burned from the catalyst during a regeneration event, or it could be alkali-metal ash or even silica particles from trace species in the fuel (see Sect. 3.6.1 of [67]). Alkali-metal levels in the fuel less than 10 ppm by weight have been found to lead to diesel particulate filter degradation [80].

Other potential fuel materials-compatibility issues exist, including lube-oil incompatibility, the fuel acting as a solvent for vehicle paint, and incompatibilities with plastic or fiberglass fuel tanks and liners. There are many important material-compatibility details to be considered when developing a new fuel blendstock.

4.5. Environmental Considerations

Fuel usage in transportation and non-road applications provides many benefits in our daily lives: from producing and distributing the food we eat, to building the communities and businesses in which we live and work, to constructing roads and bridges, to manufacturing and hauling goods for commerce, to enabling personal mobility for work and pleasure. As a result, fuel usage has increased to levels that are challenging to physically comprehend (see Section 2). Some of the environmental issues associated with this tremendous scale of fuel use are discussed below.

4.5.1. Toxicity of Fuel and Combustion Products

The first major environmental consideration is the toxicity of the fuel and its combustion products. Sometimes unburned fuel is inadvertently released into the environment; hence, it is important to know the toxicities of various fuel components, their water solubilities, and rates and strategies for biodegradation. Over the years, toxins in petroleum-derived fuels have been reduced. For example, lead (a neurotoxin) was phased out of gasoline between 1970 and 1996, and more recently the concentration of benzene (a known human carcinogen) has been limited in gasoline [4]. Some alternative fuels also have toxicity issues. The ingestion of as little as 15 ml of methanol can cause blindness, with lethal dosages in the range from 60-240 ml [81]. The jatropha plant and its seeds, which are considered a potential non-food feedstock for biofuel production, also are highly toxic. The toxicities of many alternative fuel compounds have yet to be quantified.

Fuel combustion products are released whenever fuel is burned. The primary combustion products, carbon dioxide and water, are of little or no toxicity concern, but some minor products (e.g., NO_x) are highly toxic. The levels of many toxic combustion products have been on a decreasing trend in the US since 1990 even though the total number of vehicle miles traveled, population, and energy consumption have been increasing (see Figs. 3 and 4 of [82]).

4.5.2. Climate Change

A second environmental consideration is global climate change due to human activities including the combustion of fossil fuels. Combustion produces CO_2, a GHG that inhibits radiative heat loss from the earth by absorbing infrared radiation emitted from earth, becoming vibrationally excited, and then re-radiating a fraction of this energy back to earth when it relaxes to a lower energy level. This “greenhouse effect” could play a role in the observed increase in global-average temperatures, loss of polar ice, and rising sea levels in recent decades [83]. CO_2 is not the only GHG. For example, methane (an alternative fuel) has a GHG potential 21 times that of CO_2. The link between atmospheric GHG levels and global climate change is complex and not well understood.

A large number of academic, industrial, and governmental organizations have developed models to estimate GHG emissions. Models that combine all aspects from fuel production through end-use are termed “well-to-wheels” (WTW) models. Values are generally reported in mass of CO_2 equivalent per unit volume of fuel or per unit distance traveled. Beyond WTW models, life-cycle models additionally include the emissions associated with processes to recycle vehicle components at the end of their useful lives. The specific GHG values for any fuel/engine combination are highly dependent on the modeling assumptions and the GHG-emissions estimates for the individual processes that make up a given pathway. As a result, there can be large differences in estimates obtained by different organizations. Generally, compared to petroleum-derived gasoline and diesel fuels, bio-derived fuels have a smaller GHG footprint, while coal- and oil-sands-derived fuels have larger footprints, but there can be significant differences even among the biofuels. For example, in some parts of the world, forests have been cut down to create plantations for biofuel crops such as palm oil. The GHG impacts of such land-use changes can be significant. When land-use changes are included, the GHG emissions for corn-based ethanol rise to levels much closer to those for petroleum-based fuels than ethanol from sugar cane or cellulose.

GHG emissions for electric vehicles are highly dependent on the energy source used for electricity production. Approximately 50% of the electricity generated in the US comes from coal. Electricity from coal has a larger GHG footprint than electricity from natural gas, and much larger than electricity from hydroelectric, geothermal, or nuclear energy. Of course, all of these energy sources have significant environmental aspects in addition to GHG emissions as well. When the GHG emissions of battery and electronic-component production and end-of-life recycling are taken into account in life-cycle analyses, electric vehicles are not as environmentally friendly as they might seem based on the aspect that they produce no GHG emissions at the vehicle.

4.5.3. Sustainability

The key sustainability issue for petroleum-derived fuels is that they are not being created at a rate comparable to the rate at which they are being consumed. Although the discovery of large new oil fields has diminished, proven oil reserves have continued to grow, even in the US, due to the development and deployment of new petroleum-recovery technologies. One example is the recent development of technology to extract liquids and natural gas from tight shale formations that previously were inaccessible. For bio-derived feedstocks, sustainability issues include: soil erosion and degradation, fresh water consumption, and energy return on investment (i.e., the energy content of a given amount of fuel divided by the energy required to produce the given amount of fuel). For example, estimates of the energy return on investment for corn-based ethanol are near unity (see Ch. 4 of [8]).

4.5.4. Food vs. Fuel

The final main environmental consideration is the diversion of resources from food production to fuel production. Examples of this include fuel-ethanol produced from corn, and biodiesel production from e.g., soy, canola, and palm oils. These “food vs. fuel” concerns have shifted the focus of biofuel feedstock development from conventional food crops to inedible biomass. This has led to a longer-term focus on the use of non-food crops such as camelina or jatropha as sources of triglycerides for biodiesel production.

5. FUEL SPECIFICATIONS

The specific properties that make a fuel well-suited to a given engine application have been determined over time through testing and the experience of many end-users. These properties are measured by test methods, and the set of test methods and corresponding fuel-property ranges that have been found to be acceptable for a given application are established as fuel specifications. Fuel specifications are developed to increase the likelihood that all fuels marketed for a given application will meet or exceed all relevant requirements. Ideally, a fuel specification would take into account all of the potential issues discussed previously in this article.

A fuel that meets or exceeds all relevant requirements is deemed “fit for purpose.” Fuel specifications are developed on regional, national, and/or international bases by organizations composed of representatives from vehicle makers, engine and parts manufacturers, fuel producers, and government agencies. In the United States, fuel properties must conform to ASTM specifications (ASTM D4814 [67] for gasoline and ASTM D975 [84] for diesel fuel). In Europe, most countries require fuel to conform to the CEN specifications (EN 228 for gasoline [85] and EN 590 for diesel fuel [86]). These specifications provide lower or upper limits on key fuel properties such as cetane, distillation characteristics, density, aromatic content, viscosity, and sulfur content to ensure that fuels are fit for purpose for the engines and the environments in which they will be used. The specification limits can be different for different regions/countries and can vary depending on the season (e.g., winter vs. summer). For example, the minimally acceptable value for cetane number is 40 per ASTM specifications, but 51 per CEN specifications. Differences in specifications typically reflect differences in regional engine characteristics, area climate, and environmental regulations. In the US, the Environmental

Protection Agency (EPA) and local agencies such as California Air Resources Board (CARB) have additional specifications for lower-emissions fuels sold in certain areas, and pipeline companies can set supplementary specifications for fuels transported in their pipelines. For example, some pipeline companies have limits for diesel density and pour point that are not covered by the ASTM D975 specification.

Since some specifications have a range of acceptable values while others do not have both a lower limit and an upper limit, fuels sold in the marketplace have a range of properties and compositions that reflect differences in refinery conversion units and capabilities, crude oil slates, and product slates (e.g., whether jet/kerosene and/or home-heating oil are competing for similar fuel components). Two fuel properties that vary quite a bit in the market are cetane number and aromatic content. In the US, cetane numbers range from 40 to the mid 50s. The aromatic contents of US #2 ultra-low-sulfur diesel (ULSD) fuels range from < 10 vol% to > 30 vol%. Although there is an ASTM specification maximum of 35 vol% for aromatics, it can be exceeded if the cetane index value (per ASTM D976 [87]) is 40 or higher. The aromatic values of 10 vol% and lower are found in some California fuels where the CARB #2 ULSD specification is 10 vol% maximum. However, alternative fuel formulations having aromatic contents higher than 10 vol% are allowed (and actually sold) in California, provided that the emissions of the alternative blends predicted by CARB-specified engine-test methods and models are no higher than the official 10 vol% blend [88]. In addition to wide variation in aromatic content, there is also a wide variation in the other hydrocarbon classes (n-alkanes, iso-alkanes, and mono- and poly-cycloalkanes [89]). Fuel composition and properties are also expected to change as larger quantities of alternative-fuel components derived from biofuels, oil sands, and Fischer-Tropsch type processes (from natural gas, coal, or biomass) are blended with conventional petroleum-derived fuels and enter the market. A considerable amount of testing has been conducted and more still needs to be conducted on these new blend components to relate observed engine performance with measured fuel properties and composition. The results of this testing can be used to improve the relevant fuel specification(s).

The use of detailed fuel specifications and careful engine design has largely mitigated noticeable effects of fuel-property changes on engine performance in typical applications. Nevertheless, the growing use of bio-derived and other unconventional fuels with composition and property characteristics substantially different from those of conventional petroleum-derived hydrocarbon fuels, coupled with the development of advanced high-efficiency clean-combustion engines, highlights the need for the continual evolution and improvement of fuel specifications.

5.1. Gasoline

ASTM D4814 covers specifications for 10 gasoline properties, although these do not include octane numbers (RON and MON) or antiknock index (AKI = (RON+MON)/2), which are set by gasoline refiners and marketers to meet the requirements set by the vehicle OEMs and must be clearly labeled on the fuel pumps. The properties covered are:

1. Volatility on a geographic and seasonal basis (to enable good drivability);
2. Solvent washed gum content (to limit the amount of gums formed by oxidation);
3. Oxidation stability (to provide additional protection against gum formation);

4. Water tolerance (to protect against phase separation due to dissolved water at colder temperatures – usually not a problem for blends of hydrocarbons, but can be for blends containing oxygenates);
5. Sulfur content (to limit deactivation of exhaust aftertreatment catalysts and to protect against engine wear, deterioration of engine oil, and corrosion of exhaust-system components);
6. Copper-strip corrosion (to protect against corrosion of fuel-system components due to reactive sulfur compounds);
7. Silver-strip corrosion (to protect against corrosion of silver components present in some fuel-gauge systems);
8. Lead content (to ensure that unleaded gasolines are free of lead);
9. Appearance (to ensure product is visually free of undissolved dirt, sediment, and suspended matter); and
10. Workmanship (to be free of adulterants or colorants that may make fuel unfit for purpose).

ASTM D4814 references more than 30 other ASTM standards that describe the specific test methods and equipment required to measure the gasoline properties. Specifying a property has little value unless all parties measuring the property use the same procedure and can obtain the same answer within the defined precision of the method.

ASTM D4806 [90] provides specifications for ethanol that is to be blended into gasoline. Previously, the US EPA designated certain regions as environmental non-attainment areas and required the addition of specific amounts of oxygenates in the gasoline. Recently the US Congress passed the Renewable Fuels Standard 2 (RFS2) that has delegated the authority to state and local agencies to set specific oxygenate blend-level requirements, but does require a minimum total volume of ethanol use in gasoline that escalates in time. The EPA does continue to set specifications on the maximum fraction of ethanol that can be contained in gasoline. Previously the maximum amount was 10 vol% (except for the 85 vol% E-85 ethanol blend that is approved for flexible-fuel vehicles), but in 2012 the EPA granted a waiver to allow up to 15 vol% ethanol in gasoline (E-15) for vehicle model years 2001 and newer. OEMs have expressed concerns about the 15 vol% level because some tests conducted by CRC suggest that the fuel systems in some 2001 and newer vehicles not specifically designed for E-15 may be susceptible to failure when fueled with E-15 [91] and also that older vehicles may accidentally be fueled with E-15.

For 2012, the RFS2 total ethanol requirements for the US are 13.2 billion gallons per year of corn-based ethanol and 500 million gallons of cellulosic ethanol. However, cellulosic ethanol is still in the research and development stages, and the amount produced commercially was essentially zero (see Section 2.4.1). In future years, the amount of cellulosic ethanol required continues to increase to a value of 10.5 billion gallons in 2020, but the amount of corn-based ethanol is capped at 15 billion gallons per year.

5.2. Diesel Fuel

The US diesel-fuel specification, ASTM D975 [84], covers 11 diesel-fuel properties. These include:

1. Minimum flash point (relates to safety in fuel handling and use);
2. Water and sediment (affects fuel filters and injectors);
3. Back-end volatility (related to ease of starting and smoke formation);
4. Viscosity (affects fuel spray atomization, fuel system lubrication, and fuel system leakage);
5. Ash content (can damage fuel-injection system, aftertreatment system, and cause combustion-chamber deposits);
6. Maximum sulfur content (affects aftertreatment catalysts, particulate emissions, and cylinder wear);
7. Cetane and maximum aromatic content (relates to autoignition quality and affects cold-start capability, combustion timing and performance, smoke formation, and emissions);
8. Cold temperature properties of cloud point, low temperature filterability, and cold filter plugging point (affects low temperature operability and fuel handling);
9. Carbon residue (measures coking tendency of fuel and may relate to deposit formation);
10. Copper-strip corrosion rating (indicates potential for corrosive attack on metal parts);
11. Lubricity (relates to abrasive wear of components such as fuel pump and injector; has become poorer due to removal of polar compounds during hydrotreating to meet ULSD standards)

The US RFS2 mandates the use of 1 billion gal/year of “biomass-based diesel.” Currently this predominantly is biodiesel composed of fatty acid methyl esters (FAMEs) mostly prepared from soybean vegetable oil. Several state and local governments have set mandates on the minimum fraction of biodiesel that must be blended into each gallon of diesel fuel. Issues related to the limited stabilities, low back-end volatilities, and less-than-ideal cold-temperature properties of biodiesel blends have resulted in engine manufacturers setting upper limits on biodiesel content of 5 vol% for some older engines and up to 20 vol% for newer engines. The use of FAME biodiesel has resulted in the development of ASTM D6751 [92], ASTM D7467 [93], and EN 14214 [94] specifications for the biodiesel component.

6. SUMMARY AND OUTLOOK

The production and distribution of liquid fuels from petroleum has been optimized over more than a century and a half, and the development of reciprocating internal-combustion engines to use these fuels has continued for nearly as long. Although fuel-production and engine-combustion technologies are well established (some might even say old), they continue to advance rapidly and play central roles in economy and society. This trend appears likely to continue for at least several more decades [7,95].

Significant concerns about environmental quality and energy security are currently driving the co-evolution of fuels and engines. Cost-effective, regionally produced, non-food-based, non-toxic, renewable fuels created from biological systems or solar energy and used in high-efficiency clean-combustion engines may be able to help address these concerns. These systems are being aggressively researched and developed. The optimal fuel/engine system will almost certainly be different in different areas of the world, depending on local climate, population density, resources, and myriad other factors. A great deal of research remains to be done to develop these optimal fuel/engine systems. The largest hurdle to be overcome in the area of fuels and internal-combustion engines is to meet both the tremendous scale of fuel demand and the need for high-efficiency clean-combustion engines in a manner that is cost effective and at the same time enhances environmental quality and energy security.

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