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Diesel Fuels Technical Review

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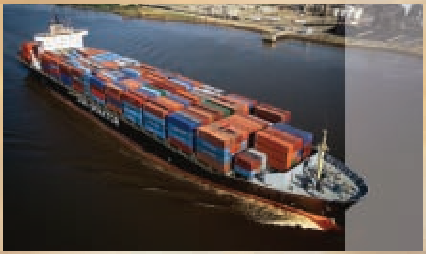

Diesel Fuels

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Introduction

The development of the internal combustion engine began in the late eighteenth century. Slow but steady progress was made over the next hundred years. By 1892, Rudolf Diesel had received a patent for a compression ignition reciprocating engine. However, his original design, which used coal dust as the fuel, did not work.

Thirty-three years earlier, in 1859, crude oil was discovered in Pennsylvania. The first product refined from crude was lamp oil (kerosene). Because only a fraction of the crude made good lamp oil, refiners had to figure out what to do with the rest of the barrel.

Diesel, recognizing that the liquid petroleum byproducts might be better engine fuels than coal dust, began to experiment with one of them. This fuel change, coupled with some mechanical design changes, resulted in a successful prototype engine in 1895. Today, both the engine and the fuel still bear his name.

The first commercial diesel engines were large and operated at low speeds. They were used to power ships, trains, and industrial plants. By the 1930s, diesel engines were also powering trucks and buses. An effort in the late ’30s to extend the engine’s use to passenger cars was interrupted by World War II. After the war, diesel passenger cars became very popular in Europe; but, they have not enjoyed comparable success in the United States yet.

Today, diesel engines are used worldwide for transportation, manufacturing, power generation, construction, and farming. The types of diesel engines are as varied as their use – from small, high-speed indirect-injection engines to low-speed direct-injection behemoths with cylinders one meter (three feet) in diameter. Their success comes from their efficiency, economy, and reliability.

The subject of this review is diesel fuel – its performance, properties, refining, and testing. A chapter in the review discusses diesel engines, especially the heavy-duty diesel engines used in trucks and buses, because the engine and the fuel work together as a system. Additionally, because environmental regulations are so important to the industry, the review examines their impact on both fuel and engine.

We hope that you will find this review a source of valuable and accurate information about a product that helps keep the world on the move.

Please note: The information in this review may be superseded by new regulations or advances in fuel or engine technology.

1 • Diesel Fuel Uses

Diesel fuel keeps the world economy moving. From consumer goods moved around the world, to the generation of electric power, to increased efficiency on farms, diesel fuel plays a vital role in strengthening the global economy and the standard of living. The major uses of diesel fuel are:

- On-road transportation
- Farming
- Rail transportation
- Marine shipping
- Off-road uses (e.g., mining, construction, and logging)
- Electric power generation
- Military transportation

In the United States, on-road[1] transportation, primarily trucks, accounted for nearly 60 percent of the diesel fuel consumed in 2004 (see Figure 1.1). Because diesel fuel is used to move goods from manufacturer to consumer, its sales are linked to the strength of the economy.[2]

Figure 1.2 shows that sales of on-road diesel fuel in the U.S. rose from 32 billion gallons in 1999 to over 37 billion gallons in 2004, an increase of nearly three percent annually. By comparison, U.S. gasoline sales in 2003 were 136 billion gallons and jet fuel sales were 24 billion gallons. Most of the diesel fuel sold in the U.S. is refined in the U.S. Relatively small volumes are imported and exported in response to market conditions in coastal or border locations.

Figure 1.1

2004 U.S. Diesel Fuel Sales

Source: U.S. Department of Energy, Energy Information Administration

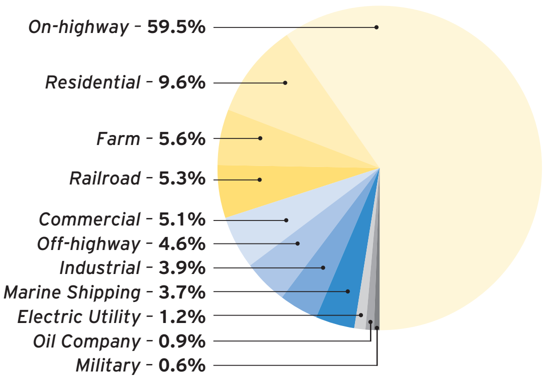
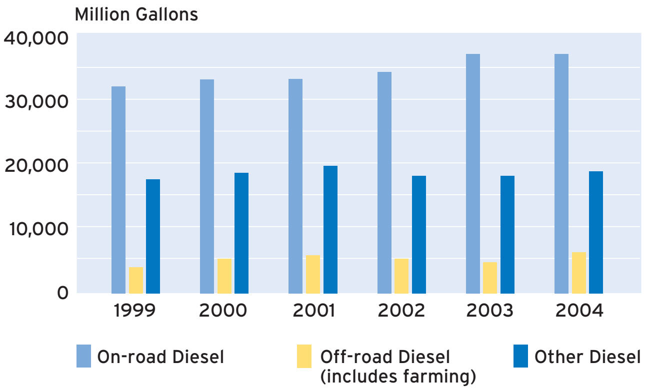


Figure 1.2

Trends in U.S. Diesel Fuel Sales 1999 - 2004

Source: U.S. Department of Energy, Energy Information Administration



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[1] Instead of "on-road," the U.S. uses the term "on-highway" in their regulations and publications, but it includes vehicular traffic capable of going on all public roads, not just highways.

[2] "U.S. Highway Fuel Demand: Trends and Prospects," American Petroleum Institute Research Study No. 084, November 1996.

FUELS FOR MARINE DIESEL ENGINES

A variety of fuels are available for marine diesel engines. There is a set of four marine distillate fuels, some of which contain small amounts of resid[3], and a set of 15 marine residual fuels in which resid is the majority constituent.

Marine fuels range in viscosity from less than one centistoke (cSt) to about 700 cSt at 50°C (122°F). (1 cSt = 1 mm^2/s.) The higher viscosity grades are preheated during use to bring their viscosity into the range suitable for injection (8 to 27 cSt). Marine fuels also contain more sulfur than on-road diesel fuel, although, in some areas and ports, only low sulfur fuels are permitted. The maximum sulfur limit varies from 1 to 4.5 percent by mass for different grades and Sulfur Emission Control Areas (SECAs).

Several organizations issue marine fuel specifications. ISO 8217 of the International Standards Organization (ISO) is the primary standard. The International Maritime Organization (IMO) also develops regulations for shipping. Among the measures adopted within IMO is MARPOL (the International Convention for the Prevention of Pollution from Ships); this is the main international convention covering the prevention of operational or accidental pollution of the marine environment by ships. MARPOL Annex VI also limits the usage of fuels to prevent air pollution.

The shipping industry prefers higher-viscosity residual fuels because they are less expensive. Although residual fuels do not burn as readily as distillate fuels, the slow speeds (60 to 200 rpm) of the large marine engines allow more time for combustion to occur.

The Energy Information Administration estimates that worldwide production of diesel fuel in 2002 was nearly 197 billion gallons.[4] In Europe and Asia, where there is a significant population of diesel-powered automobiles, the amount of diesel fuel produced exceeded the production of gasoline by just over 1.7 billion gallons.[4]

The term "diesel fuel" is generic; it refers to any fuel for a compression ignition engine. In common use, however, it refers to the fuels made commercially for diesel-powered vehicles. In the United States, this is primarily Grade No. 2-D diesel fuel. However, two other grades, Grade No. 1-D and Grade No. 4-D, are also in commercial use.

These grade designations are established by ASTM International (formerly the American Society for Testing and Materials). The grades are numbered in order of increasing density and viscosity, with No. 1-D the lightest and No. 4-D the heaviest. (See *Chapter 5 – Diesel Fuel and Biodiesel Fuel Specifications and Test Methods* for more information on examples of domestic and international diesel fuel specifications.)

RELATED PRODUCTS

Some petroleum products have similar, but not identical, physical properties and specifications. For example, No. 2 fuel oil and No. 2-GT gas turbine fuel oil are similar to No. 2-D diesel fuel. No. 1-GT gas turbine fuel oil, Jet A aviation turbine fuel, and kerosene, the product specifically sold for use in lamps and stoves, are similar to No. 1-D diesel fuel.[5] See the *Appendix* for the ASTM International specifications for these products.

The specifications for each product are developed to ensure that it is suitable for its intended use. The fuel properties needed to keep a lamp burning are not nearly as stringent as those required to keep a jet aircraft aloft. Products with similar physical properties should not be used interchangeably without a complete understanding of the requirements of their intended use.

[3] Resid or residuum is the residue that remains when crude oil is distilled.

[4] U.S. Department of Energy, Energy Information Administration, "International Energy Annual 2003."

[5] These four products represent a class of petroleum products with a boiling range of approximately 200°C to 300°C (400°F to 600°F). Following historical practice, this review uses the generic term "kerosene" to refer to this class of products and the petroleum distillate from which they are derived. However, the ASTM International specification that defines the fuel for lamps and stoves is ASTM D 3699 – *Standard Specification for Kerosine*. Dictionaries list the word as kerosene, with kerosine as an alternative spelling.

2 • Diesel Fuel and Driving Performance

Several operating characteristics influence engine performance, and their relative importance depends on engine type and duty cycle (for example, truck, passenger car, stationary generator, marine vessel, etc.). These characteristics are:

- Starting ease
- Low wear (high lubricity)
- Sufficient power
- Low temperature operability
- Low noise
- Long filter life (stability and fuel cleanliness)
- Good fuel economy
- Low emissions

Engine design has the greatest impact on most of these characteristics. However, because the focus of this publication is fuel, this chapter discusses how these characteristics are affected by fuel properties.

STARTING

Leaks and heat loss reduce the pressure and temperature of the fuel/air mixture at the end of the compression stroke (see page 73). Thus, a cold diesel engine is more difficult to start and the mixture more difficult to ignite when compared to a hot diesel engine.[1] Engines are equipped with start-assist systems that increase the air temperature to aid ignition. These controls in the diesel engine can also decrease starting engine noise, white smoke, and cranking time.

Diesel fuel that readily burns, or has good ignition quality, improves cold start performance. The cetane number (see page 4) of the fuel defines its ignition quality. It is believed that fuels meeting the ASTM D 975 *Standard Specification for Diesel Fuel Oils* minimum cetane number requirement of 40 provide adequate performance in modern diesel engines. The minimum cetane number in Europe is 51. (See *Chapter 5 – Diesel Fuel and Biodiesel Fuel Specifications and Test Methods*.) Some researchers claim that a number of modern engines can benefit from a higher cetane number when starting in very cold climates. Smoothness of operation, misfire, smoke emissions, noise, and ease of starting are all dependent on the ignition quality of the fuel. At temperatures below freezing, starting aids may be necessary regardless of the cetane number.

POWER

Power is determined by the engine design. Diesel engines are rated at the brake horsepower developed at the smoke limit.[2] For a given engine, varying fuel properties within the ASTM D 975 specification range (see page 46) does not alter power significantly.

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[1] "Diesel-Engine Management," Second edition, Robert Bosch GmbH, Stuttgart (1999).

[2] In engine terminology, brake horsepower is the usable power delivered by the engine (see sidebar, page 18). The smoke limit is the fuel-air ratio at which visible particulate emissions become excessive and are no longer acceptable.

CETANE NUMBER

The cetane number is a measure of how readily the fuel starts to burn (autoignites) under diesel engine conditions. A fuel with a high cetane number starts to burn shortly after it is injected into the cylinder; therefore, it has a short ignition delay period. Conversely, a fuel with a low cetane number resists autoignition and has a longer ignition delay period. (See page 54 for information about measuring cetane number.)

Although the cetane number of a fuel is assumed to predict its ignition delay in any engine, the actual delay represented by the cetane number is valid only for the single cylinder engine in which it was measured. The fuel's performance in other engines may differ.

A fuel's ignition delay is determined by its chemistry. In a warm engine, the delay is independent of the physical characteristics, such as volatility and viscosity of the fuel. (The Calculated Cetane Index correlations [see page 55] use density and distillation temperature properties to estimate the cetane number. However, these physical properties are used as indirect indicators of chemical properties.)

Cetane number measurement applies only to diesel fuel grades No. 1-D and No. 2-D. It is not measured for fuels containing petroleum resid (e.g., marine fuels).

However, fuel viscosity outside of the ASTM D 975 specification range causes poor atomization, leading to poor combustion, which leads to loss of power and fuel economy.

In one study, for example, seven fuels with varying distillation profiles and aromatics contents were tested in three engines. In each engine, power at peak torque and at rated speed (at full load) for the seven fuels was relatively constant.

NOISE

The noise produced by a diesel engine is a combination of combustion and mechanical noise. Fuel properties can affect combustion noise directly.

In a diesel engine, fuel ignites spontaneously shortly after injection begins. During this delay, the fuel is vaporizing and mixing with the air in the combustion chamber. Combustion causes a rapid heat release and a rapid rise of combustion chamber pressure. The rapid rise in pressure is responsible for the knock that is very audible in some diesel engines.

By increasing the cetane number of the fuel, the knock intensity is decreased by the shortened ignition delay. Fuels with high cetane numbers ignite before most of the fuel is injected into the combustion chamber. The rates of heat release and pressure rise are then controlled primarily by the rate of injection and fuel-air mixing, and smoother engine operation results.[3]

A recent development is the common rail electronic fuel injection system. The use of a common rail allows engine manufacturers to reduce exhaust emissions and, especially, to lower engine noise. (See *Chapter 6 – Diesel Engines*.)

FUEL ECONOMY

Here again, engine design is more important than fuel properties. However, for a given engine used for a particular duty, fuel economy is related to the heating value of the fuel. In North America fuel economy is customarily expressed as output per unit volume, e.g., miles per gallon. The fuel economy standard in other parts of the world is expressed as volume used per unit distance – liters per 100 kilometers. Therefore, the relevant units for heating value are heat per volume (British thermal unit [Btu] per gallon or kilojoules per liter/cubic meter). Heating value per volume is directly proportional to density when other fuel properties are unchanged. Each degree increase in American Petroleum Industry (API) gravity (0.0054 specific gravity decrease) equates to approximately two percent decrease in fuel energy content.

ASTM International specifications limit how much the heating value of a particular fuel can be increased. Increasing density involves changing the fuel's chemistry – by increasing aromatics content – or changing its distillation profile by raising the initial boiling point, end point, or both. Increasing aromatics is limited by the cetane number requirement

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[3] Khair, Magdi: "Combustion in Diesel Engines," ECOpoint Consultants, http://www.DieselNet.com

(aromatics have lower cetane numbers [see page 36]), and changing the distillation profile is limited by the 90 percent distillation temperature requirement. The API gravity at 60°F (15.6°C) for No. 2 diesel fuel is between 30 and 42. The specific gravity, at 60/60°F, and the density, at 15.6°C, are between 0.88 and 0.82. (See *Chapter 4 – Diesel Fuel Refining and Chemistry* for an explanation of fuel blending, density, and API gravity.)

Combustion catalysts may be the most vigorously promoted diesel fuel aftermarket additive (see page 81). However, the Southwest Research Institute, under the auspices of the U.S. Transportation Research Board, ran back-to-back tests of fuels with and without a variety of combustion catalysts. These tests showed that a catalyst usually made "almost no change in either fuel economy or exhaust soot levels."[4]

While some combustion catalysts can reduce emissions, it is not surprising that they do not have a measurable impact on fuel economy. To be effective in improving fuel economy, a catalyst must cause the engine to burn fuel more completely. However, there is not much room for improvement. With unadditized[5] fuel, diesel engine combustion efficiency is typically greater than 98 percent. Many ongoing design improvements to reduce emissions may have some potential for improving fuel economy. However, several modern emissions control strategies clearly reduce fuel economy, sometimes up to several percent.

WEAR

Lubricity

Some moving parts of diesel fuel pumps and injectors are protected from wear by the fuel. To avoid excessive wear, the fuel must have some minimum level of lubricity. Lubricity is the ability to reduce friction between solid surfaces in relative motion. The lubrication mechanism is a combination of hydrodynamic lubrication and boundary lubrication.

In hydrodynamic lubrication, a layer of liquid prevents contact between the opposing surfaces. For diesel fuel pumps and injectors, the liquid is the fuel itself and viscosity is the key fuel property. Fuels with higher viscosities will provide better hydrodynamic lubrication. Diesel fuels with viscosities within the ASTM D 975 specification range provide adequate hydrodynamic lubrication.

Boundary lubrication becomes important when high load and/or low speed have squeezed out much of the liquid that provides hydrodynamic lubrication, leaving small areas of the opposing surfaces in contact. Boundary lubricants are compounds that form a protective anti-wear layer by adhering to the solid surfaces.

HEATING VALUE

The heating value (also referred to as energy content) of diesel fuel is its heat of combustion; the heat released when a known quantity of fuel is burned under specific conditions. In the U.S., the heating value is usually expressed as Btu per pound or per gallon at 60°F. (International metric [SI] units are kilojoules per kilogram or per cubic meter at 15°C.) For the gross heating value, the water produced by the combustion is condensed to a liquid. For the lower net heating value, the water remains as a gas.

Because engines exhaust water as a gas, the net heating value is the appropriate value to use for comparing fuels. The heating value is customarily expressed per unit volume, specifically Btu per gallon or kilojoules per liter, because customers buy fuel by volume.

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[4] Moulton, David S. and Sefer, Norman R: "Diesel Fuel Quality and Effects of Fuel Additives," final report, PB-84-235688, Transportation Research Board, Washington DC, (May 1984) 23.

[5] Rather than repeatedly use the awkward phrase "addition of an additive," the petroleum industry coined the word "additize."

The less-processed diesel fuels of the past were good boundary lubricants. This was not caused by the hydrocarbons that constitute the bulk of the fuel, but was attributed to trace amounts of oxygen- and nitrogen-containing compounds and certain classes of aromatic compounds. Evidence for the role of trace quantities is the fact that the lubricity of a fuel can be restored with the addition of as little as 10 parts per million (ppm) of an additive.

Lubricity enhancing compounds are naturally present in diesel fuel derived from petroleum crude by distillation. They can be altered or changed by hydrotreating, the process used to reduce sulfur and aromatic contents. However, lowering sulfur or aromatics, per se, does **not** necessarily lower fuel lubricity.

The use of fuels with poor lubricity can increase fuel pump and injector wear and, at the extreme, cause catastrophic failure. Such failures occurred in Sweden in 1991 when two classes of "city" diesel (with very low sulfur and aromatics contents) were mandated. Heavy hydrotreating was needed to make these fuels. The problem was solved by treating the fuel with a lubricity additive. As regions regulate lower sulfur levels, mostly accomplished with more severe hydrotreating, the general trend is lower levels of lubricity in unfinished, unadditized fuels. The additized finished fuel in the market, however, should have adequate lubricity because of the fuel specifications in place.

Various laboratory test methods exist to determine fuel lubricity. One method widely used is the high frequency reciprocating rig (HFRR). Many regions of the world have fuel specifications based on this test method. (See *Chapter 5 – Diesel Fuel and Biodiesel Fuel Specifications and Test Methods*.)

Cleanliness

Inadequate lubricity is not the only cause of wear in diesel engine fuel systems. Diesel fuel can cause abrasive wear of the fuel system and the piston rings if it is contaminated with abrasive inorganic particles. Fuel injectors and fuel injection pumps are particularly susceptible to wear because the high liquid pressures they generate require extremely close tolerances between parts moving relative to one another.

ASTM D 975 limits the ash content of most diesel fuels to a maximum of 100 ppm. (Inorganic particles and oil-soluble, metallo-organic compounds both contribute to the ash content; but, only inorganic particles will cause wear.) The U.S. government has a tighter specification of 10 mg/L (approximately 12 ppm) for all particulate matter. However, neither specification addresses particle size. While most fuel filters recommended by engine manufacturers have a nominal pore size of 10 microns,[6] studies by the Southwest Research Institute reveal that the critical particle size for initiating significant abrasive wear in rotary injection fuel pumps and in high-pressure fuel injection systems is from six to seven microns.

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[6] 1 micron = 1 micrometer = 10^{-6} meter

However, as engine designs to reduce emissions result in higher fuel rail and injector pressures, the tighter clearances will have less tolerance for solids and impurities in the fuel. Consequently, some engine manufacturers are now specifying filters with pore size as low as two microns.

Acidity

Organic acids in diesel fuel can also cause corrosive wear of the fuel system. While this may be a significant wear mechanism for high sulfur diesel, it is less significant for low sulfur diesel because hydrotreating to reduce sulfur also destroys organic acids. With the introduction of biodiesel fuel, there is some indication that organic acids could potentially increase.

LOW-TEMPERATURE OPERABILITY

Low temperature operability is an issue with middle distillate fuels because they contain straight and branched chain hydrocarbons (paraffin waxes) that become solid at ambient winter temperatures in colder geographic areas. Wax formation can also be exacerbated by blends of biodiesel with conventional diesel fuel. Wax may plug the fuel filter or completely gel the fuel, making it impossible for the fuel system to deliver fuel to the engine.

Engine design changes to address this problem include locating the fuel pump and filter where they will receive the most heat from the engine. The practice of pumping more fuel to the injectors than the engine requires is also beneficial because the warmed excess fuel is circulated back to the tank. While the primary purpose of this recycle is to cool the injectors, it also heats the fuel in the fuel tank.

Sometimes operators may allow diesel equipment to idle in cold weather rather than turning the engine off when it is not in use. This practice is no longer allowed in certain regions. In some cases the cost of the fuel may be less than the cost of winterizing the engine; vehicles designed for low-temperature operation are usually equipped with heated fuel tanks, insulated fuel lines, and heated fuel filters.

In a refinery, there are a number of approaches to improve a fuel's low-temperature operability, such as:

- Manufacture it from less waxy crudes.
- Manufacture it to a lower distillation end point. (This excludes higher boiling waxy components with higher melting points.)
- Dilute it with a fuel with lower wax content (No. 1-D diesel fuel or kerosene).
- Treat it with a low-temperature operability additive (see page 83).

After the fuel is in the distribution system, dilution with No. 1 diesel is the most practical way to improve low-temperature performance. Additives are used to improve low-temperature filterability and lower the pour point. When they work, additives have several advantages over dilution: they are readily available in most areas of the world, treatment cost is less, and the treatment does not lower fuel density (thus heating value and fuel economy are not affected).

Low-temperature operability issues are also discussed on page 56. The tests to characterize a fuel's low-temperature operability (cloud point [ASTM D 2500], pour point [ASTM D 97], cold filter plugging point [ASTM D 6371], and low-temperature flow test [ASTM D 4539]) are discussed on page 65.

FUEL STABILITY – FILTER LIFE

Unstable diesel fuels can form soluble gums or insoluble organic particulates. Both gums and particulates may contribute to injector deposits, and particulates can clog fuel filters. The formation of gums and particulates may occur gradually during long-term storage or quickly during fuel system recirculation caused by fuel heating.

Storage stability of diesel fuel has been studied extensively because of governmental and military interest in fuel reserves. However, long-term (at ambient temperatures) storage stability is of little concern to the average user, because most diesel fuel is consumed within a few weeks of manufacture. Thermal (high-temperature) stability, on the other hand, is a necessary requirement for diesel fuel to function effectively as a heat transfer fluid. Thermal stability may become more important because diesel engine manufacturers expect future injector designs to employ higher pressures to achieve better combustion and lower emissions. The change will subject the fuel to higher temperatures and/or longer injector residence times.

Low sulfur diesel fuels tend to be more stable than their high sulfur predecessors because hydrotreating to remove sulfur also tends to destroy the precursors of insoluble organic particulates (see page 37). However, hydrotreating also tends to destroy naturally occurring antioxidants. It may be necessary for the refiner to treat some low sulfur diesel fuels with a stabilizer to prevent the formation of peroxides that are the precursors of soluble gums (see page 87).

PARAFFIN WAX

All middle distillate fuels will precipitate paraffin wax when they are cooled to a low enough temperature. Paraffin wax is a solid mixture of crystalline hydrocarbons, primarily straight chain hydrocarbons, plus some branched chain and cyclic hydrocarbons (see page 30). When it is oil-free, this wax melts in the range 40°C to 80°C (100°F to 180°F). Paraffin wax occurs naturally in all crude oils; the amount depends on the specific crude oil(s) from which it was produced and on the processing used.

As fuel is cooled, it reaches a temperature where it is no longer able to dissolve the waxy components that then begin to precipitate out of the solution. The temperature at which wax just begins to precipitate and the fuel becomes cloudy is the cloud point as measured by ASTM D 2500.

If the fuel is cooled below the cloud point, more wax precipitates. At approximately 3°C to 5°C (6°F to 10°F) below the cloud point (for fuels that do not contain a pour point depressant additive) the fuel becomes so thick it will no longer flow. This temperature is called the pour point or gel point as measured by ASTM D 97.

SMOKE

The fuel system of a diesel engine is designed and calibrated so that it does not inject more fuel than the engine can consume completely through combustion. If an excess of fuel exists, the engine will be unable to consume it completely, and incomplete combustion will produce black smoke. The point at which smoke production begins is known as the smoke limit. Most countries set standards for exhaust smoke from high-speed, heavy-duty engines. In the U.S., the opacity of smoke may not exceed 20 percent during engine acceleration mode or 15 percent during engine lugging mode under specified test conditions.

Smoke that appears after engine warm-up is an indication of maintenance or adjustment problems. A restricted air filter may limit the amount of air, or a worn injector may introduce too much fuel. Other causes may be miscalibrated fuel pumps or maladjusted injection timing. Changes made to fuel pump calibration and injection timing to increase the power of an engine can lead to increased emissions.

Because smoke is an indication of mechanical problems, California and other states have programs to test the exhaust opacity of on-road heavy-duty trucks under maximum engine speed conditions (i.e., snap idle test). Owners of trucks that fail the test are required to demonstrate that they have made repairs to correct the problem. There are also smoke regulations for ships in port.

Variation of most fuel properties within the normal ranges will not lead to the high level of particulate matter (PM) represented by smoking. The exception is cetane number; fuel with a very high cetane number can cause smoking in some engines. The short ignition delay causes most of the fuel to be burned in the diffusion-controlled phase of combustion (see page 78), which can lead to higher PM emissions.

Fuel can indirectly lead to smoking by degrading injector performance over time, when:

- Gums in the fuel are deposited on the injectors, causing sticking, which interferes with fuel metering.
- Petroleum resid or inorganic salts in the fuel result in injector tip deposits that prevent the injector from creating the desired fuel spray pattern. (Some low-speed, large diesel engines are designed to burn fuel containing large amounts of petroleum resid. These are typically used in marine and power generation applications.)
- Abrasive contaminants or organic acids in the fuel, or inadequate fuel lubricity cause excessive abrasive or corrosive injector wear.

3 • Diesel Fuel and Air Quality

THE BEGINNING

Smog is the common term for the forms of air pollution involving haze and oxidants such as ozone. Smog was identified as a serious problem in the Los Angeles Basin in the 1950s. As university scientists and government health scientists investigated the problem, they found that vehicle emissions were a significant source of smog precursors. Acting on this information, the California Legislature established emissions limits for 1966 model year cars and 1969 model year diesel trucks.

As part of a greater air quality program, U.S. federal legislation to reduce vehicular emissions was initiated with the adoption of the Clean Air Act of 1963. The first federal limits for exhaust emissions from gasoline-powered vehicles were implemented starting with the 1968 model year and from diesel-powered vehicles starting with the 1971 model year. The allowable emissions have been systematically lowered in the intervening years.

It is almost impossible to discuss motor vehicles without considering air quality. Globally, many congested urban and suburban areas fail to meet one or more local air quality standards and, in some of these areas, vehicles are responsible for a large part of the problem emissions.

This chapter explains:

- Who regulates emissions, and why and how they are regulated.
- The types of vehicle emissions and how they are formed.
- How emissions are affected by diesel fuel characteristics and how diesel fuel is being reformulated to reduce emissions.

These explanations are complicated because they involve complex regulations and science. Sometimes complete accuracy is sacrificed to keep this review as short and simple as possible. The number of acronyms used in this chapter is unavoidable; both government regulations and science heavily use them.

PROGRESS

Are the efforts of adding pollution control systems to vehicles and reformulating fuels paying off in better air quality? The answer is – *yes*[1] (see Table 3.1).

Table 3.1

National Air Pollutant Emissions Estimates (Fires and Dust Excluded) for Major Pollutants

	Millions of Tons Per Year							
	1970	1975	1980	1985	1990	1995	2000[1]	2005[2]
Carbon Monoxide (CO)	197.3	184.0	177.8	169.6	143.6	120.0	102.9	89
Nitrogen Oxides (NO_X)[3]	26.9	26.4	27.1	25.8	25.2	24.7	22.3	19
Particulate Matter (PM)[4]								
PM_{10}	12.2	7.0	6.2	3.6	3.2	3.1	2.3	2
$PM_{2.5}$[5]	NA	NA	NA	NA	2.3	2.2	1.8	2
Sulfur Dioxide (SO_2)	31.2	28.0	25.9	23.3	23.1	18.6	16.3	15
Volatile Organic Compounds (VOC)	33.7	30.2	30.1	26.9	23.1	21.6	16.9	16
Lead[6]	0.221	0.16	0.074	0.022	0.005	0.004	0.003	0.003
Totals[7]	301.5	275.8	267.2	249.2	218.2	188.0	160.2	141

1 In 1985 and 1996, EPA refined its methods for estimating emissions. Between 1970 and 1975, EPA revised its methods for estimating particulate matter emissions.

2 The estimates for 2005 are preliminary.

3 NO_X estimates prior to 1990 include emissions from fires. Fires would represent a small percentage of the NO_X emissions.

4 PM estimates do not include condensable PM or the majority of $PM_{2.5}$ that is formed in the atmosphere from "precursor" gases such as SO_2 and NO_X.

5 EPA has not estimated $PM_{2.5}$ emissions prior to 1990.

6 The 1999 estimate for lead is used to represent 2000 and 2005 because lead estimates do not exist for these years.

7 $PM_{2.5}$ emissions are not added when calculating the total because they are included in the PM_{10} estimate.

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[1] "Air Trends, National Air Pollutant Emissions Estimates for Major Pollutants," U.S. EPA, http://www.epa.gov/airtrends/econ-emissions.html

Urban air quality has improved steadily over the last thirty years. Figure 3.1[2] illustrates the trend lines for concentrations of three air pollutants – carbon monoxide, ozone, and nitrogen dioxide – in the U.S. The decreases are not uniform from year to year and may indicate the impact of meteorological fluctuations on ambient pollutant concentrations.

The improvement in urban air quality primarily occurs from the significant advances in emissions control technologies that were applied to various emission sources. For example, emissions of particulate matter and nitrogen oxides from a new, heavy-duty diesel truck in the year 2007 will be only one percent of those emitted by a similar vehicle built before emission controls were established.

Even greater improvements have been achieved for gasoline-powered cars. Similarly impressive improvements have been achieved for certain stationary sources such as refineries and power plants. In fact, from 1970 to 2004, combined air pollutant emissions from all sources in the U.S. have decreased by 54 percent. During this same period, the U.S. population increased 40 percent, energy consumption increased 47 percent, vehicle miles traveled increased 171 percent, and gross domestic product increased 187 percent.

LEGISLATION

The U.S. Clean Air Act of 1963 initiated the federal government's regulation of air pollution and has been amended in 1967, 1970, 1977, and, most recently, in 1990. The stated purpose of the act is: ". . . to protect and enhance the quality of the Nation's air resources." As the purpose suggests, the act addresses a wide range of air pollution issues, not just vehicle emissions.

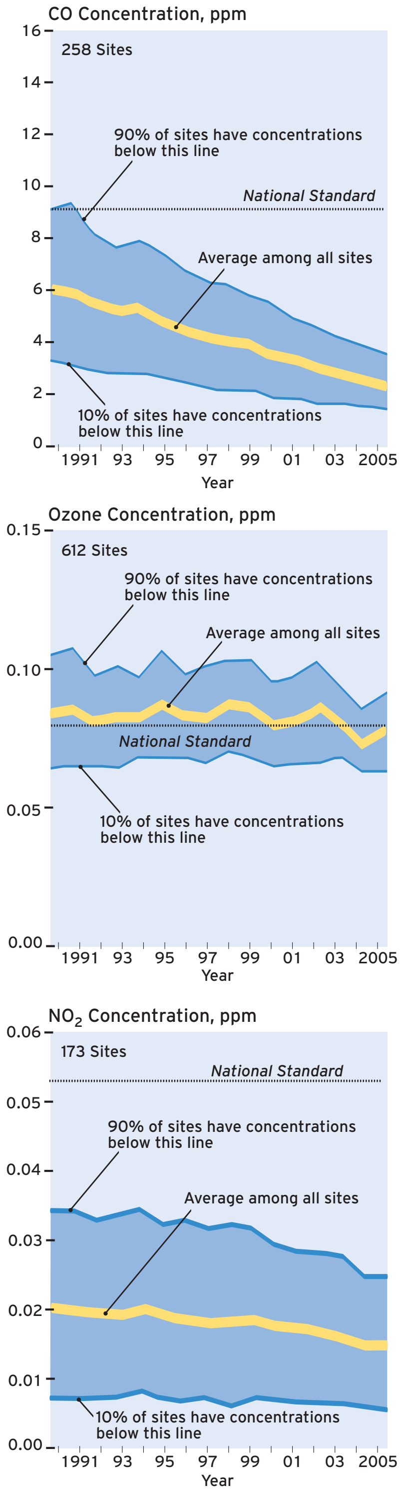
ADMINISTRATION/REGULATION

In many cases in the U.S., laws are not administered by the body that enacts them. Congress or a state legislature often assigns the administrative responsibility to a governmental agency. The 1970 amendments of the Clean Air Act created the U.S. Environmental Protection Agency (EPA) and made it responsible for implementing the requirements of the act and its amendments. California's laws covering vehicle emissions are administered by the California Air Resources Board (CARB), which was established by the legislature in 1969.

While some laws contain a lot of detail, they cannot address all the issues surrounding their application in our complex industrial society. The agency administering the law has the responsibility to write regulations, which make the legislative intent a reality. Title 40 of the Code of Federal Regulations contains the U.S. EPA regulations for environmental protection.

Figure 3.1

U.S. Air Pollutants Trend Lines



CO Concentration, ppm

Ozone Concentration, ppm

NO_2 Concentration, ppm

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[2] U.S. EPA, http://www.epa.gov/air/airtrends/aqtrnd03/

As Congress intended, the states do much of the work to carry out the provisions of the Clean Air Act and its amendments. State and local air pollution agencies hold hearings, write regulations (based on guidance from the EPA), issue permits, monitor pollution, issue notices of violations, and levy fines. It is appropriate for the states to take the lead because states and local agencies need to select and enforce the pollution control strategies that make sense for their region. Geography, weather conditions, housing patterns, regional traffic patterns, and the nature of local industry all influence pollution levels.[3]

The Clean Air Act and its amendments "... set deadlines for the EPA, states, local governments and businesses to reduce air pollution." Each state is required to develop a state implementation plan (SIP) that explains the actions it will take to meet or maintain the air quality standards set by the EPA; the EPA must approve each state's SIP. The EPA assists the states by providing scientific research, expert studies, engineering designs, and money to support clean air programs.

AIR QUALITY STANDARDS

Air pollutants are either natural or artificial airborne substances that are introduced into the environment in a concentration sufficient to have a measurable affect on humans, animals, vegetation, building materials, or visibility. From a regulatory standpoint, substances become air pollutants when the regulating agency classifies them as such. As part of the regulatory process, the U.S. Clean Air Act requires that the EPA issues a criteria document for each pollutant, detailing its adverse effects. Regulated pollutants are therefore referred to as criteria pollutants. The U.S. EPA uses information in the criteria documents to set National Ambient Air Quality Standards (NAAQS) at levels that protect public health and welfare. Table 3.2 lists the criteria pollutants and U.S. federal, California, and European Union standards. Some criteria pollutants, like carbon monoxide, are primary pollutants emitted directly by identifiable sources. Other pollutants, such as ozone, are secondary pollutants formed by reactions in the atmosphere. Particulates are of mixed origin.

Ozone

Ground-level ozone is formed by the interaction of volatile organic compounds (VOCs),[4] oxides of nitrogen (NO_x), and sunlight.[5] The role of sunlight explains why the highest

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[3] "The Plain English Guide to the Clean Air Act," EPA 400-K-93-001, U.S. EPA, Washington, DC, (April 1993).

[4] The EPA defines VOCs as all organic compounds that participate in atmospheric photochemical reactions. Because methane and ethane have negligible photochemical reactivity, the EPA does not consider them VOCs for regulatory purposes.

[5] In the stratosphere, a layer of ozone partially shields the earth from solar ultraviolet radiation. Stratospheric ozone is formed by a different mechanism than ground-level ozone.

Table 3.2

Ambient Air Quality Standards

Criteria Pollutant	Averaging Time	Maximum Average Concentration			World Health Organization
		U.S. Federal Standard	California Standard	European Union Standard*	
Ozone (O_3), ppm	1-hour/8-hour	–/0.08	0.09/0.07	–/0.10	–/100 $\mu g/m^3$
Carbon Monoxide (CO), ppm	15-minute/1-hour/ 8-hour	–/35/9	–/20/9	83/25/8.3	100/30/10 mg/m^3
Nitrogen Dioxide (NO_2), ppm	1-hour/annual	–/0.053	0.25/–	0.17/0.033	200/40 $\mu g/m^3$
Sulfur Dioxide (SO_2), ppm	1-hour/24-hour/ annual	–/0.14/0.03	0.25/0.04/–	0.29/0.10/-	–/20/– $\mu g/m^3$
Respirable Particulate Matter (PM_{10}), $\mu g/m^3$	24-hour/annual	150/50	50/20	50/40	50/20
Fine Particulate Matter ($PM_{2.5}$), $\mu g/m^3$	24-hour/annual	65/15	–/12	–/–	25/10
Lead, $\mu g/m^3$	30-day/quarterly/ annual	–/1.5/–	1.5/–/–	-/-/0.5	–
Sulfates, $\mu g/m^3$	24-hour	–	25	–	–

* EU standards specify acceptable ambient levels for ozone, nitrogen dioxide, sulfur dioxide, and respirable particulate matter (PM_{10}). European guidelines for carbon monoxide and lead are suggested by the World Health Organization.

concentrations of ozone in the atmosphere occur in the summer months and why there is a diurnal (daily) pattern to the concentrations, with the highest concentrations occurring in the afternoon and lower concentrations at night.

Ozone levels have decreased 20 percent, on average, nationwide since 1980.[6]

"Exposure to ozone has been linked to a number of health effects, including significant decreases in lung function, inflammation of the airways, and increased respiratory symptoms . . . Ozone also affects vegetation and ecosystems, leading to reductions in agricultural crop and commercial forest yields. In the United States, ground-level ozone is responsible for an estimated $500 million in reduced crop production each year."[7]

[6] "Air Trends, Ozone," U.S. EPA, http://www.epa.gov/airtrends/ozone.html

[7] "Ozone - Good Up High Bad Nearby," U.S. EPA, http://www.epa.gov/oar/oaqps/gooduphigh/

Volatile Organic Compounds

VOCs are not a criteria air pollutant, though some specific compounds are classified as toxics (see page 16). Their importance stems from their role in forming ozone. All hydrocarbons in the atmosphere are considered VOCs, as are many other types of organic compounds. This explains why so much effort is directed toward reducing hydrocarbon emissions from vehicles and stationary sources.

The main sources of global VOC emissions are vegetation (primarily tropical) (377 million metric tons carbon equivalent), fossil fuels (161 million metric tons carbon equivalent), and biomass burning (33 million metric ton carbon equivalent).[8] In the 20-year period from 1983–2002, anthropogenic VOC emissions in the U.S. decreased by 40 percent.[9] Diesel engines accounted for only approximately three percent of the anthropogenic VOC emissions in 2002 (see Figure 3.2).

Not all hydrocarbons contribute equally to ozone formation. Their reactivity depends on their chemical structure and the atmospheric conditions to which they are subjected. Under most conditions, olefins and aromatics are more reactive than paraffins.

The toxicity of organics depends on their structure. Most hydrocarbons are non-toxic at low concentrations; some low molecular weight aldehydes are carcinogenic, and some monocyclic and polycyclic aromatic hydrocarbons (PAH) are suspected or known carcinogens.

Carbon Monoxide (CO)

CO is generated primarily by combustion processes. The U.S. EPA estimates that diesel engines were responsible for approximately two percent of the anthropogenic CO emissions in 2002 (see Figure 3.3). Carbon monoxide emissions in the U.S. from 1983–2002 decreased by 41 percent along with a 65 percent decrease in ambient CO concentration.[10] CO's toxicity stems from its ability to reduce the oxygen-carrying capacity of blood by preferentially bonding to hemoglobin.

Nitrogen Dioxide (NO_2)

The air quality standard applies only to NO_2; however, where emissions are concerned, NO and NO_2 are usually analyzed and expressed as NO_x. Most (94 percent) of the NO_x emissions are anthropogenic. The EPA estimates that diesel engines generated about 32 percent of the anthropogenic NO_x emissions in 2002 (see Figure 3.4).

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[8] "Emissions of Greenhouse Gases in the United States 2003," Energy Information Administration, Department of Energy, http://www.eia.doe.gov/oiaf/1605/gg04rpt/fnote1.html

[9] "Air Trends, September 2003 Report: National Air Quality and Emissions Trends Report, 2003 Special Studies Edition," U.S. EPA, http://www.epa.gov/air/airtrends/aqtrnd03/

[10] "Air Trends, September 2003 Report: National Air Quality and Emissions Trends Report, 2003 Special Studies Edition," U.S. EPA, http://www.epa.gov/air/airtrends/aqtrnd03/

While NO is non-toxic by itself, it contributes to ozone formation. "NO_2 can irritate the lungs and lower resistance to respiratory infection . . . "[11] Under some conditions, NO_x is also an important precursor to particulate matter.

Sulfur Dioxide (SO_2)

SO_2 is primarily produced by the combustion of fuels containing sulfur. Facilities (stationary sources) that burn fuel oil and coal are the major source of ambient SO_2. On-road and off-road engine fuels are estimated to be the source of less than three percent of the total SO_2 emissions, and this contribution will further decline because of the mid-2006 implementation of the U.S. EPA's ultra-low sulfur diesel fuel regulations and similar sulfur limits in Europe and many other countries.

SO_2 is a moderate lung irritant. Along with NO_x, it is a major precursor to acidic deposition (acid rain).

Particulate Matter (PM_{10} and $PM_{2.5}$)

PM_{10} is particulate matter with a particle size less than or equal to 10 microns (0.0004 inch), and $PM_{2.5}$ has a particle size less than or equal to 2.5 microns (0.0001 inch). The EPA estimates that fugitive dust from roads (largely from wearing of vehicle tires, brakes, and roadway surfaces) accounts for nearly 60 percent of the total PM_{10} nationwide. Less than two percent of PM_{10} is attributed to on-road and off-road engines, but the percentage is higher in urban areas where there is less dust and more combustion sources. Particulates from diesel engines include primary carbon particles and secondary sulfate and nitrate aerosols formed from SO_2 and NO_x.

After reviewing the scientific evidence of the health effects of particulate matter, the EPA established standards for $PM_{2.5}$. The EPA found that while coarse and fine particles can increase respiratory symptoms and impair breathing, fine particles are more likely to contribute to serious health effects. Most of the particulate emissions from diesel engines are significantly smaller than 2.5 microns.

Figure 3.2

Emissions Sources:
2002 National Manmade VOC Emissions
16,544,000 short tons

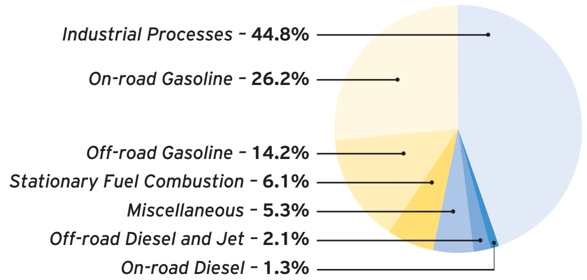


Figure 3.3

Emissions Sources:
2002 National Manmade Carbon Monoxide Emissions
112,049,000 short tons

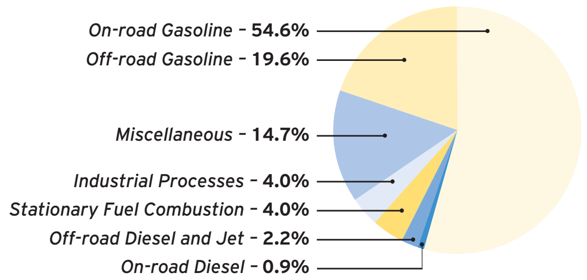
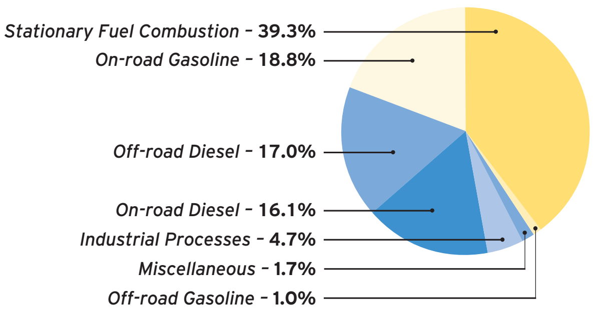


Figure 3.4

Emission Sources:
2002 National Manmade Nitrogen Oxide Emissions
21,102,000 short tons



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[11] "Air Trends, September 2003 Report: National Air Quality and Emissions Trends Report, 2003 Special Studies Edition," U.S. EPA, http://www.epa.gov/air/airtrends/aqtrnd03/

DIESEL EXHAUST TOXICITY

The potential of diesel exhaust to cause adverse health effects in people is controversial. However, several regulatory and non-regulatory agencies have concluded that exposure to diesel exhaust does increase the risk of adverse health effects, including lung cancer.

The International Agency for Research on Cancer (IARC) concluded that the evidence for diesel exhaust as a cause of cancer was sufficient in animals, but limited in humans. As a result, they categorized diesel exhaust as a potential human carcinogen (Category 2A).[13]

The National Institute of Occupational Safety and Health (NIOSH) reached the same conclusion, recommending that whole diesel exhaust be regarded as a potential cause of cancer.

The U.S. EPA and the California Air Resources Board have both concluded that exposure to diesel exhaust increases risks to respiratory health and lung cancer. Particulate matter in diesel exhaust was classified as a toxic air contaminant in California in 1998.

Air Toxics

The toxic air pollutants listed by the Clean Air Act Amendments of 1990 included: benzene, polycyclic organic matter (POM),[12] acetaldehyde, formaldehyde, and 1,3-butadiene. Of this group, only POM is found in diesel fuel. Diesel exhaust contains POM and possibly trace amounts of the other toxic pollutants.

VEHICLE EMISSIONS: SOURCES

When hydrocarbon fuel is burned with the correct amount of air in a diesel engine, the benign gases that are left are predominately water vapor, carbon dioxide, and nitrogen; carbon dioxide is a greenhouse gas. However, deviations from this ideal combustion lead to the production of some VOCs, CO, NO_x, SO_2, and PM.

Diesel engines are substantial emitters of PM and NO_x, but only small emitters of CO and VOCs. Gasoline engines are the greatest emitters of CO and substantial emitters of VOCs and NO_x, but only modest emitters of PM measured by mass.

Diesel engines are designed to run lean (i.e., with excess oxygen) and they do not emit much carbon monoxide or unburned hydrocarbons. Because diesel fuel has a much higher boiling range than gasoline (and consequently a much lower volatility), evaporative VOC emissions are not a problem.

Oxides of Nitrogen

Air is 78 percent nitrogen by volume. Diesel engines mainly produce NO_x by "burning" a small amount of the nitrogen in the air that is drawn into the cylinder. At the high temperatures encountered in a diesel combustion chamber, nitrogen combines with oxygen to form NO_x. The formation of NO_x becomes significant at approximately 1,600°C (2,900°F) and increases rapidly as the temperature rises above this threshold.

Any organic nitrogen in the fuel also contributes to NO_x emissions; but, this source is negligible compared to nitrogen in the air. Combustion chamber deposits also increase NO_x emissions slightly. The deposits are believed to raise the combustion temperature because they act as thermal insulators, reducing heat loss to the combustion chamber walls.

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[12] Polycyclic organic matter (POM) consists of polycyclic aromatic hydrocarbons (PAH), including benzo(a)pyrene, their nitrogen analogs, and a small number of oxygen-containing polycyclic organic matter compounds.

[13] "Volume 46 Diesel and Gasoline Engine Exhausts and Some Nitroarenes," World Health Organization, International Agency for Research of Cancer, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, http://monographs.iarc.fr/ENG/Monographs/vol46/volume46.pdf

Particulate Matter

PM emissions are mainly the result of the heterogeneous nature of diesel combustion. When fuel is injected into the hot compressed air in the combustion chamber, local regions develop that are fuel-rich and oxygen deficient. Because of the high temperature and pressure in the combustion chamber, the fuel may start to break down before it has a chance to mix with air and burn normally. These high-temperature cracking reactions (pyrolysis) lead to the formation of carbonaceous soot particles. Unburned or partially burned fuel can condense on the surfaces of these particles, increasing their size and mass. Finally, these particles can stick together (agglomerate) to create larger chains, which can be seen as visible smoke.

Diesel exhaust NO_x and PM are linked by the nature of diesel combustion. Efforts to reduce PM by increasing combustion efficiency lead to higher combustion temperatures, thus, higher NO_x emissions. Lowering NO_x formation by lowering combustion temperature leads to less complete combustion and, thus, higher PM emissions. The challenge for diesel engine designers is to reduce emissions of NO_x and PM simultaneously. (See *Chapter 6 – Diesel Engines* for a discussion of emissions reduction technology.)

VEHICLE EMISSIONS: LIMITS

Unlike passenger cars, in which the engine and vehicle are both produced by a single company, most heavy-duty diesel engines and vehicles are manufactured by separate companies. In addition, the vehicle manufacturers often use engines from several different sources. To simplify the qualification process, regulatory agencies have elected to apply heavy-duty diesel emission standards to engines rather than vehicles.

The U.S. EPA set limits for emissions from heavy-duty diesel engines starting with the 1971 model year. Table 3.3 lists the U.S. federal, European, and Japanese standards for NO_x and PM emissions from heavy-duty highway engines from the mid-1990s onward. Most of the countries not covered in Table 3.3 adopt some version of these regulations. California sets its own limits on diesel emissions, which are generally the same as or more restrictive than U.S. federal standards. Additional standards exist for diesel buses, off-road diesels, marine diesels, railroad diesels, and light-duty (passenger car or small trucks) diesels.

UNITS OF DIESEL ENGINE EMISSIONS

Kilowatts (kW) and brake horsepower (bhp) are units of power. By convention, the power output of an engine is measured as brake power. The adjective "brake" indicates that it is the power developed at the engine's drive shaft, which is less than the power developed inside the engine's cylinders. It is equal to the indicated power, delivered from the expanding combustion gas in the cylinder to the piston, minus all losses, which include friction, heat lost to the coolant, pulling air into the engine, and driving engine accessories.

A kilowatt-hour (kW-hr) or brake horsepower-hour (bhp-hr) is a unit of work (energy); it is the work done when the engine's shaft exerts one kilowatt (or brake horsepower) for one hour. Expressing engine emissions as mass of emissions per unit of engine work (either grams/kW-hr or grams/bhp-hr) allows the use of a single standard for engines of all sizes. A larger engine generates a higher volume of exhaust and a higher absolute amount of emissions than a smaller engine, but it also can produce more work.

continued on next page

Table 3.3

Selected U.S., European, and Japanese Heavy-Duty Highway Diesel Engine Emission Standards for NOx and PM

Year	U.S. Federal[1]		European Union		Japan	
	NO_x (g/bhp-hr)*	PM (g/bhp-hr)*	NO_x (g/kW-hr)	PM (g/kW-hr)	NO_x (g/kW-hr)	PM (g/kW-hr)
1994	5.0	0.10	8.0 (Euro I)	0.36	7.8	0.95
1996	"	"	7.0 (Euro II)	0.25	"	"
1998	4.0	0.10	"	0.15	"	"
1999	"	"	"	–	4.5	0.25
2001	"	"	5.0 (Euro III)	0.10**	"	"
2002	2.5	0.10	"	"	"	"
2005	"	"	3.5 (Euro IV)	0.02**	3.0	0.10
2007	0.20	0.010	"	"	"	"
2009	"	"	2.0 (Euro V)	0.02**	"	"

1 Due to differences in the test cycles used to determine emissions, it is not possible to directly compare standards between different regulatory agencies.

* 1 g/bhp-hr = 1.341 g/kW-hr

** European PM standards are reported using the European steady-state cycle prior to 2001, and the European transient cycle thereafter.

Exhaust emissions are very dependent on how an engine is operated. To standardize the test conditions, each regulatory agency requires that exhaust emissions be measured while the engine is operated according to a specified speed-time cycle on an engine dynamometer. The EPA Transient Test Procedure includes segments designed to mimic congested urban, uncongested urban, and freeway driving along with a cold start and a hot start. The European test cycle includes both transient and steady-state operation. The current Japanese regulatory cycle is based on a 13-mode steady-state test.

In addition to NO_x and PM standards, emissions of non-methane hydrocarbons (NMHC), a subset of VOC, carbon monoxide, and visible smoke are also regulated.[14] NMHC participates in photochemical reactions with NO_x to form ground-level ozone. Because NO_x and NMHC are linked in ozone formation, it makes sense to view them as one category rather than two. Therefore, in addition to the absolute limits on NO_x emissions, recent regulations have also incorporated standards for combined NO_x + NMHC emissions.

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[14] Methane is not included with all hydrocarbons because it is considered to have negligible photochemical reactivity in the atmosphere.

VEHICLE EMISSIONS: FUTURE LIMITS

The most recent U.S. and European emissions limits for on-highway heavy-duty diesels have become so stringent that further dramatic reductions in NO_x, PM, CO, and NMHC emissions may not be as practical or effective as in the past. Emissions standards for off-highway vehicles are typically significantly less stringent, and so will likely continue to be substantially reduced over the next decade. Therefore, rather than focusing on reduced emissions standards for new engines, regulatory agencies may adopt alternative strategies.

One possible strategy is the revision of regulatory test cycles. The primary intent of a test cycle is to reproduce the full range of operating conditions representative of engine operation in the real world. As engine technology and driving patterns change, test cycles must be revised to ensure accurate representation of real-world emissions. Generally, test cycles become increasingly challenging with each revision. There has also been a substantial effort over the last several years to establish a global standard test cycle, which can be used to qualify all engine and vehicle types for all countries.

Traditionally, regulation of engine emissions (particularly in the case of heavy-duty diesel) ends when the engine is sold to the end user. To ensure that vehicles are not polluting excessively, in-use testing may be carried out to monitor vehicle emissions under real-world conditions. In 1998, California instituted a heavy-duty vehicle inspection program to regulate smoke emissions from in-use heavy-duty diesel engines. The U.S. EPA plans to implement a similar program for NMHC, CO, NO_x, and PM on a nationwide basis starting with the 2007 model year. Various other in-use monitoring programs are in place or being developed in other areas of the world as well.

In cases where in-use monitoring shows a vehicle's emissions exceed applicable regulations, appropriate repairs will be necessary. In the U.S., the EPA requires manufacturers to guarantee heavy-duty engine emissions control systems for a minimum of 10 years/ 435,000 miles "useful life" for model year 2004 and newer engines.

A challenge associated with improving emissions from heavy-duty diesels arises from their long service life. Typical on-highway heavy-duty diesels are extremely durable, and often enjoy service lifetimes of well over 1,000,000 kilometers (621,000 miles) between major overhauls. As a consequence, it may take many years for new emissions regulations to have a significant impact while older, high-emissions engines are gradually replaced by newer low-emissions engines.

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The emissions of light-duty diesel and gasoline-powered vehicles are also expressed as mass per unit of work, but the units are grams per kilometer or grams per mile. There are two reasons why these units are not appropriate for heavy-duty diesel engines.

First, heavy-duty diesel emissions standards apply to the engine, not to the vehicle. Because the engine is not tested in a vehicle, expressing the emissions per kilometer or per mile would require a number of assumptions.

Second, there is much more variation in the sizes and loads of diesel vehicles than gasoline vehicles. Using per-kilometer or per-mile standards would penalize large trucks hauling heavy loads, even when they are more emissions-efficient.

The urban bus fleet is of particular concern in this regard, as buses usually operate in highly congested urban areas (where air quality may often be poor) and bus engines are normally overhauled multiple times, which results in extremely long average service life. Many regulatory agencies have therefore implemented programs to retrofit older urban buses with new emissions-reducing exhaust aftertreatment technologies (see *Chapter 6 – Diesel Engines* for more information on exhaust aftertreatment) at the time of a major overhaul. Such retrofitting programs have been highly effective, sometimes decreasing overall criteria emissions by as much as 90 percent.

Concern about carbon dioxide emissions and their relationship to global warming has lead to increased use of diesel engines in light-duty passenger cars, trucks, vans, and sport utility vehicles. Diesels have become especially popular in Western Europe, where at one time, tax incentives made diesel vehicles much more financially attractive than gasoline vehicles. These tax incentives are being reduced, but diesel passenger vehicles remain popular. By the end of 2004, the majority of new passenger cars sold in Western Europe were diesel powered.[15] The inherent fuel efficiency of the diesel engine, relative to the gasoline engine, results in substantially lower emissions of CO_2 per kilometer driven. However, light-duty diesel engines still emit substantially more NO_x and PM than their gasoline counterparts, and face some difficulty meeting current and upcoming emissions standards. (As of the 2006 model year, none of the light-duty diesel passenger cars offered for sale in the U.S. were able to meet California emissions regulations.) As light-duty diesel emissions control technology advances, the diesel passenger car will be cleaner and become a viable option in the U.S.

VEHICLE EMISSIONS: DIESEL FUEL EFFECTS

Advances in heavy-duty engine design have produced very large reductions in NO_x and PM emissions, and it is expected that future advances in engine technology will reduce emissions even more. The composition of diesel fuel has traditionally had much less influence on emissions; however, reformulated diesel fuels have played a modest role in achieving needed emissions reductions. The most important fuel parameters in this regard are sulfur, cetane number, density, aromatics, and volatilty.

Sulfur

The sulfur content of diesel fuel affects PM emissions because some of it in the fuel is converted to sulfate particulates in the exhaust. The fraction converted to PM varies from one engine to another, but reducing sulfur decreases PM linearly (up to a point – sulfur is not the only source of PM) in almost all engines. For this reason, and to enable some

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[15] Press release PI-4745, Robert Bosch Company, December 2004.

exhaust aftertreatment devices, the U.S. EPA limited the sulfur content of on-road diesel fuel to 15 ppm starting in 2006 (see *Ultra-Low Sulfur Diesel Fuel* in this chapter). Since 2005, the European Union has limited diesel sulfur content to 50 ppm and will further limit sulfur content to 10 ppm in 2009, Japan limited sulfur to 10 ppm in 2007.

Cetane Number

Increasing the cetane number improves fuel combustion, reduces white smoke on startup, and tends to reduce NO_x and PM emissions. NO_x seems to be reduced in all engines, while PM reductions are engine-dependent. These cetane number effects also tend to be non-linear in the sense that increasing the cetane number produces the greatest benefit when starting with a relatively low cetane number fuel.

Density

Changes in fuel density affect the energy content of the fuel brought into the engine at a given injector setting. Reducing fuel density tends to decrease NO_x emissions in older technology engines that cannot compensate for this change. Emissions from modern engines, with electronic injection and computer control, are not influenced by the density of the fuel.[16]

Aromatics

Most studies indicate that reducing total aromatics has no effect on the emissions of HC and PM. However, reducing total aromatics from 30 percent to 10 percent reduces NO_x emissions. Studies done on the influence of polynuclear aromatic hydrocarbons show that reducing the di- and tri-aromatics reduces emissions of HC, PM, and NO_x.[17]

Volatility

T_{95} is the temperature at which 95 percent of a particular diesel fuel distills in a standardized distillation test (ASTM D 86). Reducing T_{95} decreases NO_x emissions slightly, but increases hydrocarbon and CO emissions. PM emissions are unaffected.[18]

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[16] Lee, Robert, Hobbs, Christine H., and Pedley, Joanna F.: "Fuel Quality Impact on Heavy Duty Diesel Emissions: A Literature Review," Document Number 982649, SAE Technical Papers, http://www.sae.org/technical/papers/982649/

[17] Technology Transfer Network Clearinghouse for Inventories & Emissions Factors 1970 – 2002, "Average annual emissions, all criteria pollutants in MS Excel – July 2005. Posted August 2005," U.S. EPA, http://www.epa.gov/ttn/chief/trends/index.html

[18] Technology Transfer Network Clearinghouse for Inventories & Emissions Factors 1970 – 2002, "Average annual emissions, all criteria pollutants in MS Excel – July 2005. Posted August 2005," U.S. EPA, http://www.epa.gov/ttn/chief/trends/index.html

ULTRA-LOW SULFUR DIESEL FUEL

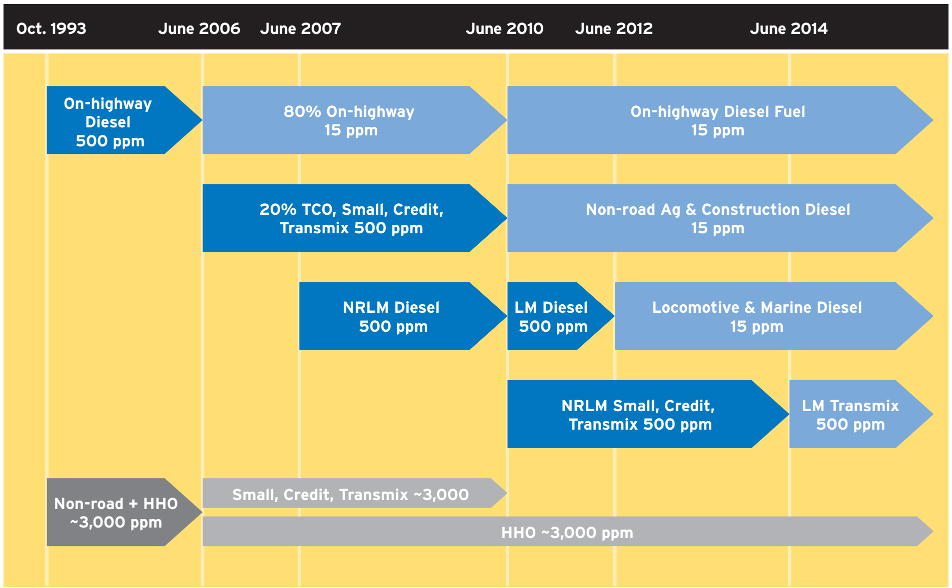
In the past, diesel engine manufacturers have produced engines to meet the increasingly stringent emissions standards through improvements to the combustion process itself. In order to meet additional regulatory standards (U.S. 2007+, Europe 2009+), most new diesel engines will need to employ some type of advanced exhaust aftertreatment technology (see *Emission Reduction Technologies* in *Chapter 6 – Diesel Engines*). Because most exhaust aftertreatment devices are very sensitive to sulfur (some devices can be permanently damaged by prolonged exposure to fuel sulfur levels as low as 50 ppm), vehicles so equipped must use ultra-low sulfur diesel (ULSD) fuel, officially designated as S15 in the ASTM diesel fuel standard. The term "ultra-low sulfur diesel" may refer to different levels of sulfur in different parts of the world. However, for the purposes of this review, ULSD refers to diesel fuel containing less than 15 ppm sulfur in the U.S. and less than 10 ppm sulfur in Europe and the Asia-Pacific region.

In California, the Air Resources Board (ARB) has regulated an additional requirement. All diesel fuel sold in this state must have an aromatics content of 10 mass percent or less. Alternatively, a fuel supplier can test and certify a fuel with higher aromatics level, if emissions are equivalent to those of a specific reference fuel with a 10 mass percent aromatics level. In that case, other fuel properties (cetane number, sulfur, nitrogen, aromatics, and polynuclear aromatics) are recorded. Fuel marketed under this certification must be within the recorded limits of these five properties.

ULSD became widely available in Western Europe and Japan (10 ppm sulfur maximum) starting in 2005; the U.S. (15 ppm sulfur maximum) followed in 2006. Full transition to ULSD will occur over a period of several years, with 100 percent of on-highway and off-road diesel meeting ULSD specifications by 2009 in Europe and by 2010–2014 in the U.S. While ULSD enables use of advanced exhaust aftertreatment technology on new diesel engines, it is also fully compatible with, and will help reduce sulfate emissions from, existing older technology diesel engines. Figure 3.5 illustrates the EPA timeline for the on-highway and non-road diesel fuel sulfur control standards in the U.S.

Figure 3.5

Timeline: EPA On-highway and Non-road Diesel Sulfur Production Standards 2010 and Beyond*

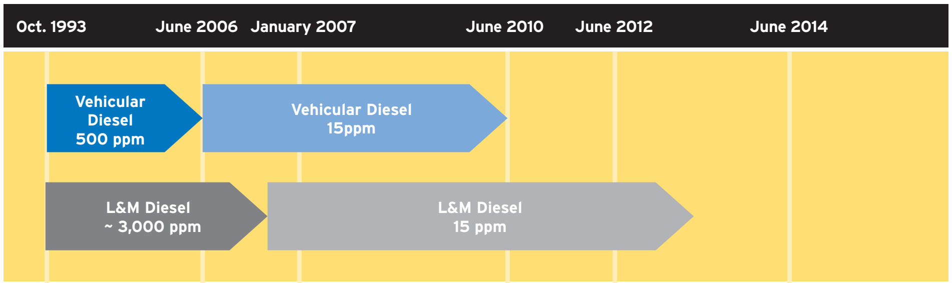


* This figure illustrates the timeline for the final highway and non-road diesel fuel sulfur control programs.
NR = Non-road, LM = Locomotive & Marine, HHO = Home Heating Oil, TCO = Temporary Compliance Option.

As shown in Figure 3.6, the California ARB has developed a timeline for vehicular, non-road agricultural, and construction vehicle emissions standards for their state.

Figure 3.6

Timeline: CARB Diesel Fuel Sulfur Production Standards*



* This figure illustrates the final timeline for 15 ppm CARB vehicular diesel fuel and
CARB locomotive & marine (L&M) diesel fuel.

U.S. FEDERAL DIESEL FUEL EXCISE TAX

The federal government imposes an excise tax, currently $0.244 per gallon, on diesel fuel. However, certain fuel uses are tax-exempt or subject to a reduced rate. These uses include: heating, farming, use by state or local governments or non-profit educational organizations, and boats engaged in fishing or transportation.

Because Congress believed that there was considerable evasion of this tax, the Omnibus Budget Reconciliation Act of 1993 changed some of the diesel tax procedures. Under the Internal Revenue Service (IRS) regulations, the tax is levied on diesel fuel that is removed from a terminal's truck loading rack unless the fuel is dyed red.

Red-dyed diesel fuel may be used only for non-taxable purposes. Anyone who knowingly sells or uses dyed diesel fuel for taxable purposes or who willfully alters the concentration of dye in diesel fuel is subject to a minimum $10 per gallon penalty. The 1993 act gives the IRS authority to enforce the diesel fuel tax, including the authority to inspect terminals, dyes, dyeing equipment, and fuel storage facilities, and to stop, detain, and inspect vehicles.

DIESEL FUEL DYEING IN THE U.S.

In the U.S., a confusing situation for both refiners and purchasers of diesel fuel has arisen because the IRS and the EPA require the addition of red dye to certain classes of diesel fuel. Each agency requires adding the dye to a different class of fuel, at a different concentration, and for a different reason such as:

- The EPA wants to identify diesel fuel with high-sulfur content to ensure that it is not used in on-road vehicles.
- The IRS wants to ensure that tax-exempt high-sulfur and low-sulfur diesel fuel are not used for taxable purposes.

The EPA Requirements

U.S. EPA regulations require "visible evidence of the presence of red dye" to identify high-sulfur fuels when they leave the refinery. In practice, this requires refiners to add a level of red dye that is equivalent to no more than 0.75 pounds/1,000 bbl (ptb) (2.14 mg/L) of a solid Solvent Red 26 dye standard. Solvent Red 26 was chosen as the standard because it is a unique chemical available in pure form. Diesel fuels are actually dyed with liquid concentrates of Solvent Red 164 because this dye is more fuel soluble and less costly than the standard. Solvent Red 164 is a mixture of isomers that are very similar to Solvent Red 26, except the former incorporates hydrocarbon (alkyl) chains to increase its solubility in petroleum products.

Any red dye observed in the fuel of a vehicle in on-road use triggers a measurement of the fuel's sulfur content. Penalties are assessed based on the actual sulfur content of the fuel, rather than simply on the presence of dye.

As of June 2012, only heating oil will require red dye for EPA purposes. By then, on-road, non-road, locomotive, and marine diesels will all be ULSD.

The Internal Revenue Service (IRS) Requirements

U.S. IRS regulations require that tax-exempt diesel fuels, both high-sulfur and low-sulfur, have a minimum level of a Solvent Red 164 dye that is spectrally equivalent to 3.9 ptb of the Solvent Red 26 dye standard. This level of dye is more than five times the amount required by the EPA regulations. The IRS contends that the high dye level is necessary to allow detection of tax evasion even after five-fold dilution of dyed fuel with undyed fuel.

4 • Diesel Fuel Refining and Chemistry

Diesel fuel is made from petroleum. All petroleum crude oils are composed primarily of hydrocarbons of the paraffinic, naphthenic, and aromatic classes. Each class contains a very broad range of molecular weights.

Out of the ground, crude oil can be as thin and light-colored as apple cider or as thick and black as melted tar. Thin crude oils have relatively low densities and thus, high API gravities (see sidebar). In the U.S., light crudes are called high-gravity crude oils; conversely, thick and heavy crude oils with relatively high densities are low-gravity crude oils. Outside of the U.S. the terminology “light crude” refers to a low-density crude oil and “heavy crude” to a high-density crude oil.

Refining is the process of converting crude oil into high value products. The most important are transportation fuels: gasoline, jet fuel, and diesel fuel. Other products include liquefied petroleum gas (LPG), heating fuel, lubricating oil, wax, and asphalt. High-gravity crude oils contain more of the lighter products such as gasoline and generally have lower sulfur and nitrogen contents, which makes them easier to refine. However, modern refining processes are capable of turning low-gravity crude oils into high value products. Refining low-gravity crude oils requires more complex and expensive processing equipment, more processing steps, and more energy; therefore, costs more. The price difference between high-gravity and low-gravity crude oils reflects a portion of the refining cost difference.

REFINING PROCESSES

Today’s refinery is a complex combination of interdependent processes, the result of a fascinating intertwining of advances in chemistry, engineering, and metallurgy. These processes can be divided into three basic categories:

- **Separation processes** The feed to these processes is separated into two or more components based on a physical property, usually boiling point. These processes do not otherwise change the feedstock. The most common separation process in a refinery is distillation.
- **Upgrading processes** These processes improve the quality of a material by using chemical reactions to remove compounds present in trace amounts that give the material an undesirable quality. Otherwise the bulk properties of the feedstock are not changed. The most commonly used upgrading process for diesel fuel is hydrotreating to remove sulfur.
- **Conversion processes** These processes fundamentally change the molecular structure of the feedstock, usually by “cracking” large molecules into small ones (e.g., catalytic cracking and hydrocracking).

DENSITY AND GRAVITY

Density (ρ) is the mass of a unit volume of material at a selected temperature. For example, the density of water is 0.9990 grams per cubic centimeter (g/cm^3) at 60°F (15.6°C). Relative density (RD) – also called specific gravity – is the ratio of the density of the material at a selected temperature to the density of a reference material at a selected temperature. For the relative density of petroleum crudes and products in the U.S., the reference material is water and both temperatures are 60°F.

$$RD\ (60/60°F) = \frac{\rho \text{ sample } (60°F)}{\rho \text{ water } (60°F)}$$

Outside of the U.S., relative density is also defined with respect to water. The temperature for both the water and the material is 15°C.

The U.S. petroleum industry often uses API gravity instead of relative density. The following equation relates API gravity, in degrees API (°API), to relative density.

$$°API = \frac{141.5}{RD\ (60/60°F)} - 131.5$$

While API gravity measurements may be made on liquids at temperatures other than 60°F, the results are always converted to the values at 60°F, the standard temperature.

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API gravity is an arbitrary scale developed by the American Petroleum Institute in the early years of the petroleum industry. Density had been used as a primary indicator of quality for liquid products. However the higher value products have lower densities. The API gravity scale was constructed so that API gravity increases inversely to density; therefore, higher value products have higher API gravities. While the densities of most petroleum products are less than one, the API gravity scale was constructed so that most values are between 10 and 70.

Distillation

Distillation is by far the most important and widely used separation process in a petroleum refinery. In large part, petroleum products are defined by their boiling range, and distillation is the process used to separate crude oil or other wide boiling range mixtures into products with narrower boiling ranges.

Crude oil is made up of many thousands of components from light gases that boil below ambient temperature, to very heavy materials that cannot be distilled even at temperatures above 550°C (1,000°F).[1]

In crude petroleum distillation, hot oil is pumped into a distillation column and the lightest hydrocarbons present[2], usually propane and butane, rise to the top of the column and are removed. Since gasoline is a little heavier, it does not rise quite so high and is drawn off from the side of the column. Kerosene and diesel, the next heavier products, are drawn off at successively lower points on the column. The products that are obtained directly from crude oil distillation are called straight-run products (e.g., straight-run diesel). The material that is too heavy to vaporize under atmospheric distillation conditions is removed from the bottom of the column (atmospheric bottoms).

The atmospheric bottoms can be fractionated further by a second distillation carried out under reduced pressure. The lower pressure in the distillation column allows some of the heavier components to be vaporized and collected. This process is called vacuum distillation; the overhead product is called vacuum gas oil (VGO), and the bottoms product is called vacuum resid.

Because of the distillation profile of the typical crude, refining by distillation alone has not been able to meet market demand for light fuel products since the early 1900s. It yields too much heavy products and not enough light products. In addition, the quality of light products produced by distillation alone is often poor. The petroleum refiner uses the upgrading and conversion processes to match the barrel to the market.

Upgrading Process

Hydroprocessing (hydrogen treating process) is a generic term for a range of processes that use hydrogen with an appropriate catalyst[3] to remove undesired components from a refinery stream. The processes run the gamut from mild conditions that remove reactive

[1] In distillation discussions, the terms “light” and “heavy” are used for “lower boiling” and “higher boiling.” They do not refer to the density of materials; although, generally, a lower boiling material is also less dense than a high boiling material.

[2] Methane and ethane are often present in crude oil as it comes out of the ground. These lightest compounds are removed before the crude oil is transported by pipeline or tanker.

[3] A catalyst is a material that accelerates or otherwise facilitates a chemical reaction without undergoing a permanent chemical change itself.

compounds like olefins, some sulfur, nitrogen and oxygen compounds (hydrofinishing), to more severe conditions that saturate aromatic rings and remove almost all sulfur and nitrogen compounds (hydrotreating).

Conversion Process

Hydrocarbons with higher boiling points (the larger molecules in the distillation bottoms) can be broken down (cracked) into lower boiling hydrocarbons by subjecting them to very high temperatures. The discovery of this process (thermal cracking) offered a way to correct the mismatch between supply and demand. Since 1913, thermal cracking has been used to increase gasoline production. Although by today's standards, the quality and performance of these earlier cracked products was low, they were sufficient for the engines of the day.

Eventually heat was supplemented by a catalyst, transforming thermal cracking into catalytic cracking. Catalytic cracking produces higher quality products than thermal cracking. There are many variations on catalytic cracking, but fluid catalytic cracking (FCC) is probably the most widely used conversion process, worldwide. Most of the liquid product from FCC eventually goes into gasoline; however, one product stream, light cycle oil (LCO), is often blended into diesel fuel. Before blending, LCO undergoes subsequent hydrotreating to lower sulfur content which makes the LCO more stable and suitable for adding to diesel fuel. To meet the 15 ppm sulfur requirement, LCO undergoes subsequent hydrotreating to lower sulfur content.

Hydrocracking is another major conversion process. It is similar to catalytic cracking because it uses a catalyst, but the reactions take place under a high pressure of hydrogen. The primary feed to the hydrocracking unit is VGO. During hydrocracking, large VGO molecules are cracked into smaller molecules by either cleaving carbon-carbon bonds or by plucking out sulfur and nitrogen atoms from -carbon-sulfur-carbon- and -carbon-nitrogen-carbon- molecular linkages. Because of the high hydrogen pressure used in hydrotreating, hydrogen is added to the fragmented molecular ends formed by either cleaving carbon-carbon bonds or by extracting sulfur and nitrogen linkage atoms; in addition, rings of some aromatic compounds are saturated with hydrogen during the hydrocracking process. Kerosene and diesel form a large percentage of the product from a hydrocracker. These products are nearly void of sulfur and nitrogen and are enriched in hydrogen.

THE MODERN REFINERY

A schematic layout of a modern, fully integrated refinery is shown in Figure 4.1. (The diesel fuel related streams are highlighted in blue.) Crude oil is fed to the distillation column where straight-run naphtha, light and heavy gasoline, chemical naphtha, kerosene, and diesel are separated at atmospheric pressure.

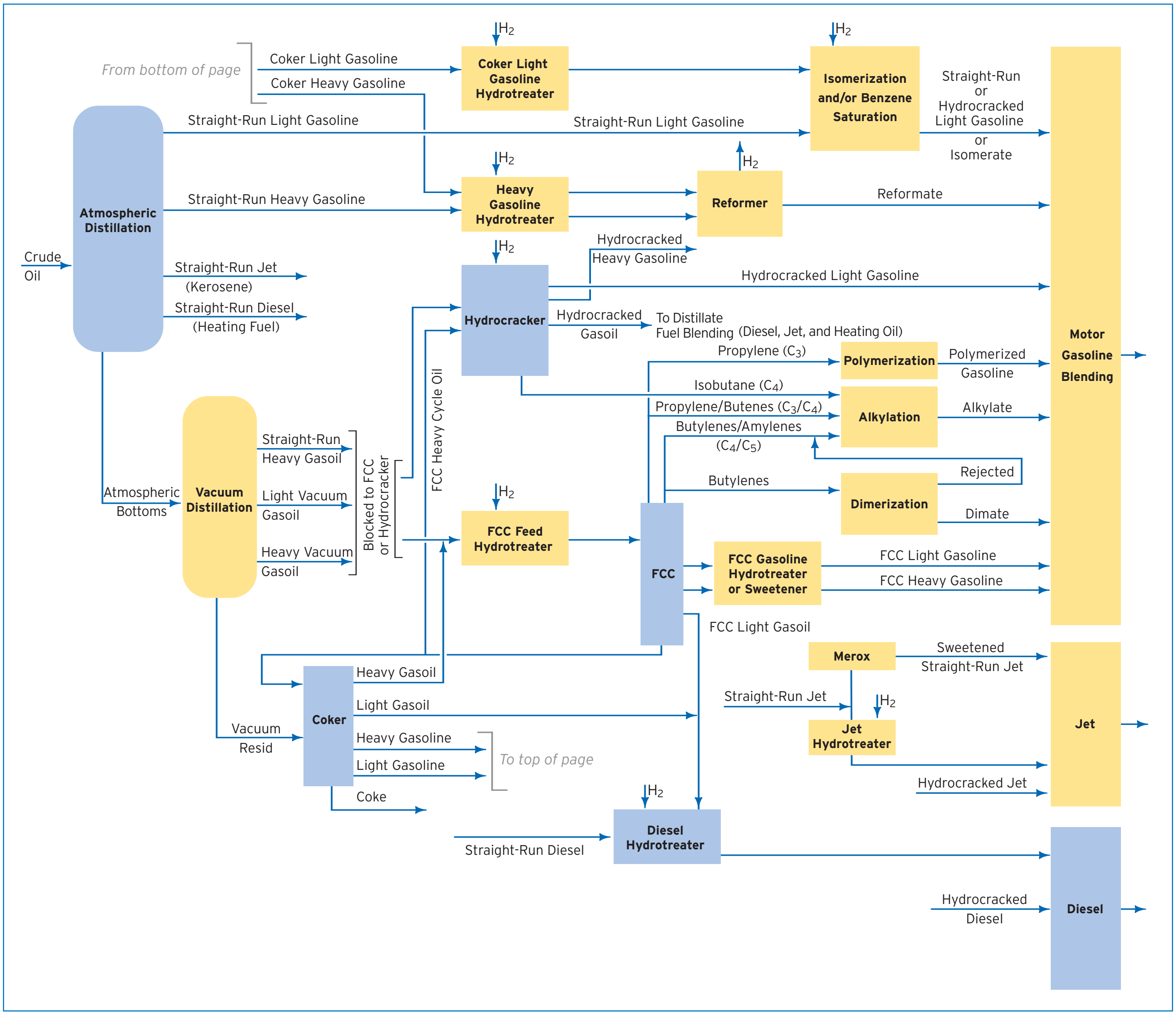


Figure 4.1
The Modern Refinery

The VGO obtained from vacuum distillation of the atmospheric bottoms are fed to either the FCC unit or the hydrocracker. The VGO may be hydrotreated to reduce sulfur and nitrogen to levels that will improve the performance of the FCC process.

Previously, the vacuum resid might have been used as a low value, high-sulfur fuel oil for onshore power generation or marine fuel. But to remain competitive, refiners must wring as much high value product as possible from every barrel of crude. As a result, the vacuum resid may be sent to a resid conversion unit, such as a resid cracker, solvent extraction unit, or coker. These units produce additional transportation fuel or gas oil, leaving an irreducible minimum of resid or coke.

BLENDING

The diesel fuel produced by a refinery is a blend of all the appropriate available streams: straight-run product, FCC light cycle oil, and hydrocracked gas oil. The straight-run diesel may be acceptable as is, or may need minor upgrading for use in diesel fuel prepared for off-road use. To meet the 15 ppm sulfur limit, all the streams used to prepare diesel fuel need hydrotreating to lower the sulfur concentration.

The refiner must blend the available streams to meet all performance, regulatory, economic, and inventory requirements. Sophisticated computer programs have been developed to optimize all aspects of refinery operation, including the final blending step. Refineries are optimized for overall performance, not just for the production of diesel fuel.

The refiner really has limited control over the detailed composition of the final diesel blend. It is determined primarily by the composition of the crude oil feed, which is usually selected based on considerations of availability and cost. While the chemical reactions that occur in the conversion processes involve compositional changes, they are not specific enough to allow for much tailoring of the products. Yet, despite these limitations, refineries daily produce large volumes of on-test products. Truly, a remarkable achievement!

ABOUT HYDROCARBONS

Hydrocarbons are organic compounds composed entirely of carbon and hydrogen atoms. There are four major classes of hydrocarbons: paraffins, naphthenes, olefins, and aromatics. Each class is a family of individual hydrocarbon molecules that share a common structural feature, but differ in size (number of carbon atoms) or geometry. The classes also differ in the ratio of hydrogen to carbon atoms and in the way the carbon atoms are bonded to each other.

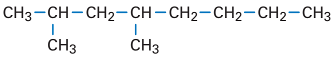
Paraffins

n-Paraffin

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

n-Decane $C_{10}H_{22}$

Isoparaffin



$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_2-CH_3$

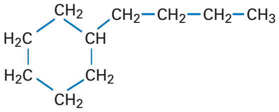
2,4-Dimethyloctane $C_{10}H_{22}$

Paraffins have the general formula $C_nH_{2n}+_2$, where “n” is the number of carbon atoms (carbon number) in the molecule. There are two subclasses of paraffins: normal paraffins and isoparaffins.

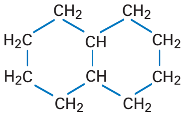
Normal paraffins have carbon atoms linked to form chain-like molecules, with each carbon – except those at the ends – bonded to two others, one on either side. Isoparaffins have a similar carbon backbone, but they also have one or more carbons branching off from the backbone. Normal decane and 2,4-dimethyloctane have the same chemical formula, $C_{10}H_{22}$, but different chemical and physical properties. Compounds like this, with the same chemical formula but a different arrangement of atoms, are called structural isomers.

Naphthenes

Naphthenes



Butylcyclohexane $C_{10}H_{20}$



Decalin $C_{10}H_{18}$

Naphthenes[4] have some of their carbon atoms arranged in a ring. The naphthenes in diesel fuel have rings of five or six carbons. Sometimes two or more rings are fused together, with some carbons shared by adjacent rings. Naphthenes with one ring have the general formula C_nH_{2n}.

Olefins

Olefin

$CH_2=CH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

1-Decene $C_{10}H_{20}$

Olefins are similar to paraffins but have fewer hydrogen atoms and contain at least one double bond between a pair of carbon atoms. Olefins rarely occur in crude oil; they are formed by certain refinery processes. Like paraffins, olefins with four or more carbons can exist as structural isomers. Olefins with one double bond have the general formula C_nH_{2n}, the same as naphthenes.

---

[4] Naphthene is the term used in the petroleum industry to describe saturated cyclic or ring hydrocarbons. The same compounds are also known as cycloalkanes and cycloparaffins.

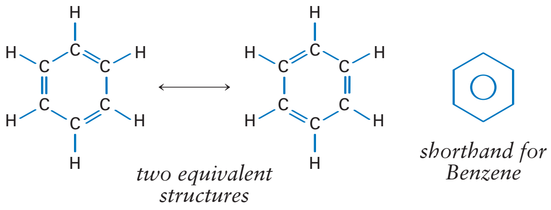
Aromatics

As with naphthenes, some of the carbon atoms in aromatics are arranged in a ring, but they are joined by aromatic bonds, not the single bonds found in naphthenes. Aromatic hydrocarbon rings contain six carbon atoms. Benzene is the simplest aromatic compound. The benzene structure was originally conceptualized as two equivalent structures with alternating single and double bonds. Each structure continually transformed itself into the other as the double bonds flipped back and forth between different pairs of carbon atoms. Now, we know that all the carbon to carbon bonds in benzene are equivalent. The shorthand representation of benzene is a hexagon with a circle inside representing the aromatic bonds. One-ring aromatics have the general formula C_nH_{2n-6}. Polycyclic aromatics are compounds with two or more aromatic rings. These rings are fused together, with some carbons being shared by adjacent rings.

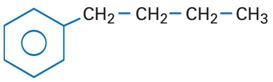
Paraffins and naphthenes are classified as saturated hydrocarbons because no more hydrogen can be added to them without breaking the carbon backbone. Aromatics and olefins are classified as unsaturated hydrocarbons. They contain carbon to carbon double bonds or aromatic bonds that can be converted to single bonds by adding hydrogen atoms to the adjacent carbons. When straight-chain olefins are saturated with hydrogen, they become paraffins. When aromatics are completely saturated with hydrogen, they become naphthenes; when they are partially saturated, they become cyclic olefins.

Some molecules contain structural features characteristic of two or more hydrocarbon classes. For example, a molecule could contain an aromatic ring, a naphthenic ring, and a paraffinic chain. How should this molecule be classified? Chemists have established a hierarchy of hydrocarbon structural features, with aromatics at the top, followed by olefins, naphthenes, and paraffins. A compound with features of more than one class is placed in the class highest in the hierarchy. So, in our example, the molecule is classified as an aromatic.

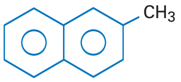
Aromatic Compounds



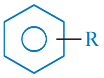
Benzene C_6H_6



Butylbenzene $C_{10}H_{14}$



2-Methylnaphthalene $C_{11}H_{10}$
Polycyclic aromatic or polynuclear aromatic



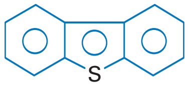
Substituted Aromatic:

R *represents an alkyl (hydrocarbon) group that can be bonded to any one of the carbons in the benzene ring.*

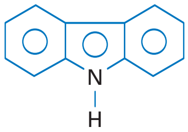
OTHER COMPOUNDS

While carbon and hydrogen are the predominant elements in crude oil, small amounts of sulfur, nitrogen, and oxygen are also present. These elements are called heteroatoms (“other” atoms). Molecules containing heteroatoms are not classified as hydrocarbons. Typical examples found in diesel fuel include dibenzothiophene and carbazole. Although these compounds are present in small amounts, they play a large role in determining certain fuel properties.

Heteroatomic Compounds



Dibenzothiophene



Carbazole

DIESEL FUEL CHEMISTRY

Figure 4.2 illustrates a typical carbon number distribution for No. 2-D diesel fuel, and Figure 4.3 shows a typical distillation profile. Diesel fuel is a very complex mixture of thousands of individual compounds, most with carbon numbers between 10 and 22. Most of these compounds are members of the paraffinic, naphthenic, or aromatic class of hydrocarbons; each class has different chemical and physical properties. Different relative proportions of the three classes is one of the factors that make one diesel fuel different from another. The following discussion explains how properties of the three classes influence the properties of the whole fuel and affect its performance in a diesel engine.

Figure 4.2

Typical Carbon Number Distribution – No. 2-D Diesel Fuel

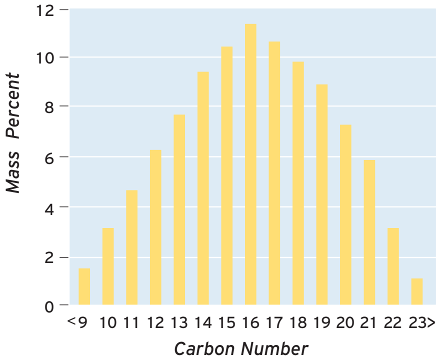
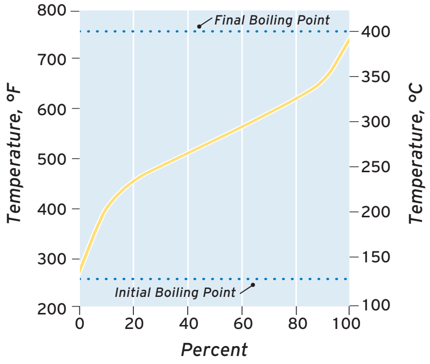


Figure 4.3

Typical Distillation Profile – No. 2-D Diesel Fuel



Hydrocarbon Properties

Table 4.1 lists the boiling points and freezing points of typical diesel fuel hydrocarbons.

Table 4.1

Boiling Point and Freezing Point of Representative Diesel Fuel Hydrocarbons

Compound	Chemical Formula	Hydrocarbon Class	Boiling Point, °C/°F	Freezing Point, °C/°F
Naphthalene	$C_{10}H_8$	Aromatic	218/424	80/176
Tetralin	$C_{10}H_{12}$	Aromatic	208/406	-35/-31
cis-Decalin	$C_{10}H_{18}$	Naphthene	196/385	-43/-45
1,3-Diethylbenzene	$C_{10}H_{14}$	Aromatic	181/358	-84/-119
n-Butylcyclohexane	$C_{10}H_{20}$	Naphthene	181/358	-75/-103
n-Pentylcyclopentane	$C_{10}H_{20}$	Naphthene	181/358	-83/-117
Decane	$C_{10}H_{22}$	n-Paraffin	174/345	-30/-22
Anthracene	$C_{14}H_{10}$	Aromatic	341/646	215/419
1-Pentylnaphthalene	$C_{15}H_{18}$	Aromatic	306/583	-24/-11
n-Nonylcyclohexane	$C_{15}H_{30}$	Naphthene	282/540	-10/14
n-Decylcyclopentane	$C_{15}H_{30}$	Naphthene	279/534	-22/-8
n-Pentadecane	$C_{15}H_{32}$	n-Paraffin	271/520	10/50
2-Methyltetradecane	$C_{15}H_{32}$	Isoparaffin	265/509	-8/18
1-Decylnaphthalene	$C_{20}H_{28}$	Aromatic	379/714	15/59
n-Tetradecylbenzene	$C_{20}H_{34}$	Aromatic	354/669	16/61
n-Tetradecylcyclohexane	$C_{20}H_{40}$	Naphthene	354/669	25/77
n-Pentadecylcyclopentane	$C_{20}H_{40}$	Naphthene	353/667	17/63
Eicosane	$C_{20}H_{42}$	n-Paraffin	344/651	36/97
2-Methylnonadecane	$C_{20}H_{42}$	Isoparaffin	339/642	18/64

Boiling Points

For compounds in the same class, boiling point increases with carbon number. For compounds of the same carbon number, the order of increasing boiling point by class is isoparaffin, n-paraffin, naphthene, and aromatic. The boiling point difference (60° to 80°C or 100° to 150°F) between isoparaffins and aromatics of the same carbon number is larger than the boiling point difference (about 20°C or 35°F) between compounds of the same class that differ by one carbon number. Thus, the compounds that boil at about 260°C (500°F), the middle of the diesel fuel boiling range, might be C_{12} aromatics, C_{13} naphthenes, C_{14} n-paraffin, and C_{15} isoparaffins.

THERMAL EXPANSION

Like all liquids, diesel fuel expands slightly in volume as its temperature increases. The coefficient of thermal expansion measures the rate of the expansion. A typical value of the coefficient of thermal expansion for diesel fuel is 0.00083 per degree Celsius (0.00046 per degree Fahrenheit). Using this value, 1.000 gallon of diesel fuel at -7°C (20°F) will expand to 1.037 gallons at 38°C (100°F).

Freezing Point

Freezing points (melting points) also increase with molecular weight, but they are strongly influenced by molecular shape. Molecules that fit more easily into a crystal structure have higher freezing points than other molecules. This explains the high melting points of n-paraffins and unsubstituted aromatics, compared to the melting points of isoparaffins and naphthenes of the same carbon number.

Density

Table 4.2 lists density and heat of combustion (heating value) for some representative diesel fuel hydrocarbons. For compounds of the same class, density increases with carbon number. For compounds with the same carbon number, the order of increasing density is paraffin, naphthene, and aromatic.

Table 4.2

Density and Heat of Combustion for Representative Diesel Fuel Hydrocarbons

Compound	Hydrocarbon Class	Carbon Number	Density, 20°C, g/cm^3	Net Heat of Combustion, 25°C, kJ/kg	Net Heat of Combustion, 25°C, Btu/gal
Naphthalene	Aromatic	10	1.175	38,854	163,800
Tetralin	Aromatic	10	0.9695	40,524	140,960
1,3-Diethylbenzene	Aromatic	10	0.8639	41,384	128,270
n-Butylcyclohexane	Naphthene	10	0.7992	43,717	124,500
n-Pentylcyclopentane	Naphthene	10	0.7912	43,585	123,720
Decane	n-Paraffin	10	0.7301	44,236	115,880
2,2-Dimethyloctane	Isoparaffin	10	0.7245	44,145	114,750
Anthracene	Aromatic	14	1.251	38,412	172,410
n-Nonylbenzene	Aromatic	15	0.8558	42,147	129,410
n-Nonylcyclohexane	Naphthene	15	0.816	43,431	127,150
n-Decylcyclopentane	Naphthene	15	0.811	43,545	126,710
n-Pentadecane	n-Paraffin	15	0.7684	43,980	121,250
n-Tetradecylbenzene	Aromatic	20	0.8549	42,482	130,310
n-Tetradecylcyclohexane	Naphthene	20	0.825	43,445	128,590
n-Pentadecylcyclopentane	Naphthene	20	0.8213	43,524	128,260
Eicosane	n-Paraffin	20	0.7843	43,852	123,400

Heating Value

For compounds with the same carbon number, the order of increasing heating value by class is aromatic, naphthene, and paraffin on a weight basis. However, the order is reversed for a comparison on a volume basis, with aromatic highest and paraffin lowest.

This same trend holds with fuels (see Table 4.3). Lighter (less dense) fuels, like gasoline, have higher heating values on a weight basis, whereas the heavier (more dense) fuels, like diesel, have higher heating values on a volume basis.

Table 4.3

Typical Density and Net Heating Value of Different Fuels

Fuel	Density, 15°C, g/cm^3	Net Heating Value			
		Btu/lb	Btu/gal	kJ/kg	kJ/L
Regular Gasoline	0.735	18,630	114,200	43,330	31,830
Premium Gasoline	0.755	18,440	116,200	42,890	32,390
Jet Fuel	0.795	18,420	122,200	42,850	34,060
Diesel Fuel	0.850	18,330	130,000	42,640	36,240

Cetane Number

Cetane number also varies systematically with hydrocarbon structure (see Table 4.4). Normal paraffins have high cetane numbers that increase with molecular weight. Isoparaffins have a wide range of cetane numbers, from about 10 to 80. Molecules with many short side chains have low cetane numbers; whereas those with one side chain of four or more carbons have high cetane numbers.

Naphthenes generally have cetane numbers from 40 to 70. Higher molecular weight molecules with one long side chain have high cetane numbers; lower molecular weight molecules with short side chains have low cetane numbers.

Aromatics have cetane numbers ranging from zero to 60. A molecule with a single aromatic ring with a long side chain will be in the upper part of this range; a molecule with a single ring with several short side chains will be in the lower part. Molecules with two or three aromatic rings fused together have cetane numbers below 20.

Table 4.4

Cetane Number of Representative Diesel Fuel Hydrocarbons

Compound	Hydrocarbon Class	Chemical Formula	Cetane Number
n-Decane	n-Paraffin	$C_{10}H_{22}$	76
n-Pentadecane	n-Paraffin	$C_{15}H_{32}$	95
n-Hexadecane*	n-Paraffin	$C_{16}H_{34}$	100
n-Eicosane	n-Paraffin	$C_{20}H_{42}$	110
3-Ethyldecane	Isoparaffin	$C_{12}H_{26}$	48
4,5-Diethyloctane	Isoparaffin	$C_{12}H_{26}$	20
Heptamethylnonane*	Isoparaffin	$C_{16}H_{34}$	15
8-Propylpentadecane	Isoparaffin	$C_{18}H_{38}$	48
7,8-Diethyltetradecane	Isoparaffin	$C_{18}H_{38}$	67
9,10-Dimethyloctane	Isoparaffin	$C_{20}H_{42}$	59
Decalin	Naphthene	$C_{10}H_{18}$	48
3-Cyclohexylhexane	Naphthene	$C_{12}H_{24}$	36
2-Methyl-3-cyclohexylnonane	Naphthene	$C_{16}H_{32}$	70
2-Cyclohexyltetradecane	Naphthene	$C_{20}H_{40}$	57
1-Methylnaphthalene*	Aromatic	$C_{11}H_{10}$	0
n-Pentylbenzene	Aromatic	$C_{11}H_{16}$	8
Biphenyl	Aromatic	$C_{12}H_{10}$	21
1-Butylnaphthalene	Aromatic	$C_{14}H_{16}$	6
n-Nonylbenzene	Aromatic	$C_{15}H_{24}$	50
2-Octylnaphthalene	Aromatic	$C_{18}H_{24}$	18
n-Tetradecylbenzene	Aromatic	$C_{20}H_{34}$	72

* Primary reference material for cetane number scale

Viscosity

Viscosity is primarily related to molecular weight and not so much to hydrocarbon class. For a given carbon number, naphthenes generally have slightly higher viscosities than paraffins or aromatics.

Hydrocarbon Class/Fuel Properties Relationship

Table 4.5 summarizes the relationships between hydrocarbon class and fuel properties. Normal paraffins have excellent cetane numbers, but very poor cold flow properties and low volumetric heating values. Aromatics have very good cold flow properties and volumetric heating values, but very low cetane numbers. Isoparaffins and naphthenes are intermediate, with values of these properties between those of normal paraffins and aromatics.

Table 4.5

Relationship of Hydrocarbon Class Properties to Fuel Properties

Fuel Property	Normal Paraffin	Isoparaffin	Naphthene	Aromatic
Cetane Number	+	0/+	0/+	0/–
Low-Temperature Operability	–	0/+	+	+
Volumetric Heating Value	–	–	0	+

\+ Indicates a positive or beneficial effect on the fuel property
0 Indicates a neutral or minor effect
– Indicates a negative or detrimental effect

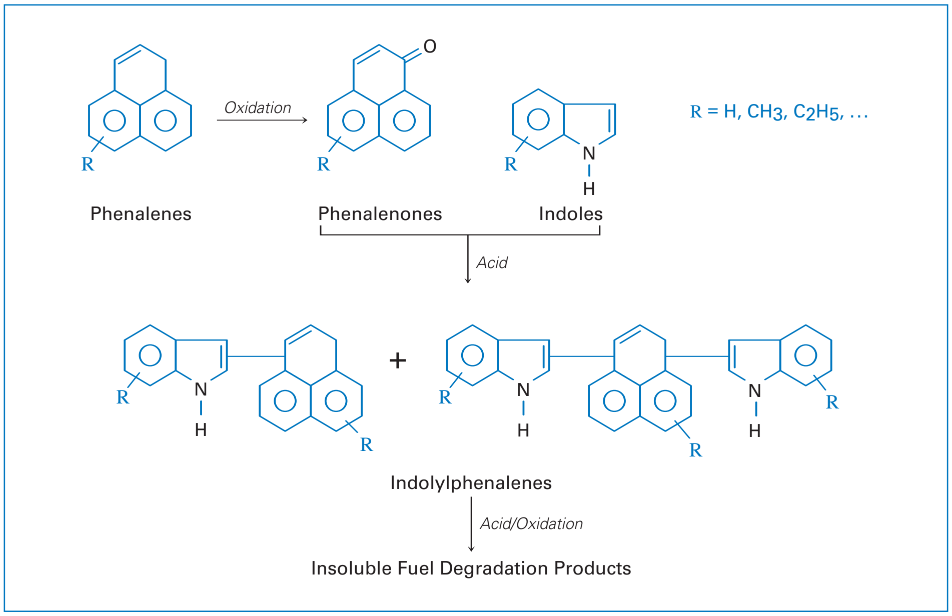
CHEMISTRY OF DIESEL FUEL INSTABILITY

For the most part, instability involves the chemical conversion of precursors to species of higher molecular weight with limited fuel solubility and tend to be nitrogen- and sulfur-containing compounds, organic acids, and reactive olefins. The conversion process often involves oxidation of the precursors. Certain dissolved metals, especially copper, contribute by functioning as oxidation catalysts. Fuel solvency also plays a role, because the development of insolubles is always a function of both the presence of higher molecular weight species and the capacity of the fuel to dissolve them.

One well-established mechanism by which insolubles are formed is the acid-catalyzed conversion of phenalenones and indoles to complex indolylphenalene salts (see Figure 4.4).[5] Phenalenones are formed by oxidation of certain reactive olefins; indoles occur naturally in certain blend components of diesel fuel. The required organic acid is either present in a blend component or is generated by the oxidation of mercaptans to sulfonic acids. This mechanism can be interrupted by various means, e.g., by omitting acidic species and/or their precursors from the fuel blend, by destroying the precursors by hydrotreating, or by adding antioxidant or basic stabilizer additives. ASTM D 6748 *Standard Test Method for Determination of Potential Instability of Middle Distillate Fuels Caused by the Presence of Phenalenes and Phenalenones (Rapid Method by Portable Spectrophotometer)* discusses the measurement of phenalenes and phenalenones in diesel fuel to determine the potential for storage instability.

Figure 4.4

Sequence of Reactions Leading to Formation of Insolubles in Diesel Fuel



[5] Adapted from Pedley, *et al.*: "Storage Stability of Petroleum-Derived Diesel Fuel," *Fuel* 68, (1989) 27-31.

Contrary to intuition, two fuels that, by themselves, have good stability may form a less stable blend when they are combined. In this case, each fuel contains some of the precursors needed for the formation of higher molecular weight species. Only when the fuels are mixed are all the precursors available, enabling the conversion to proceed.

Another example of an unexpected interaction involves 2-ethylhexyl nitrate (EHN) (diesel ignition improver or cetane number improver). The addition of EHN to a fuel or the blending of fuels, one of which contains EHN, may increase thermal instability because the decomposition of EHN promotes the reactions that lead to higher molecular weight species.

As of the date of this publication, there is not enough experience with S15 diesel fuel stability. (S15 is the ASTM international designation for diesel fuel with 15 ppm or less sulfur.) Since many of the species that can form particulates are removed during hydrotreatment, it is believed that S15 diesel will have excellent thermal stability and not react with the cetane number improver ethylhexyl nitrate. However, there is some concern that S15 diesel, without the natural oxidation inhibitors which are removed by hydrotreating, may form peroxides during long-term storage.

BIODIESEL FUEL

In the United States, biodiesel fuel production has grown from approximately one half-million gallons (just under 2 million liters) in 1999 to an estimated 75 million gallons (284 million liters) in 2005. This was approximately 0.2 percent of total diesel production in 2005.[6] The main reason for the interest is that biodiesel is a renewable source of energy.

In general usage, the term biodiesel covers a variety of materials made from vegetable oils, recycled cooking greases or oils, or animal fats. The definition of the term "biodiesel" is being debated, but for the purposes of the publication the following ASTM International definition applies: "a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100".[7]

Vegetable oils and animal fats consist of three fatty acids – hydrocarbon chains of varying lengths, bonded to a glycerol molecule (see Table 4.6). This structure is commonly known as a triglyceride. Table 4.6 lists a variety of fatty acids, indicating hydrocarbon chain length and the number of carbon-carbon double bonds.

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[6] Biodiesel, A Role for SAE," *SAE Motor Vehicle Council*, (31 March 2006).

[7] ASTM International, ASTM D 6751 *Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels*, www.astm.org

Table 4.6

Component Fatty Acids of Some Vegetable and Seed Oils and Fats, and Some Animal Fats

Common Names	Caproic 6:0*	Caprylic 8:0	Capric 10:0	Lauric 12:0	Myristic 14:0	Palmitic 16:0	Palmitoleic 16:1	Stearic 18:0	Oleic 18:1	Linoleic 18:2	Linolenic 18:3	Arachidic 20:0	Gadoleic 20:1	Behenic 22:0	Erucic 22:1
Canola[1]	–	–	–	–	–	4	–	2	56	26	10	–	–	–	–
Cottonseed	–	–	–	–	–	27	–	2	18	51	Trace	–	–	–	–
Peanut	–	–	–	–	–	13	–	3	38	41	Trace	–	3	–	1
Olive	–	–	–	–	–	10	–	2	78	7	–	–	–	–	–
Rice Bran	–	–	–	–	–	16	–	2	42	37	1	–	–	–	–
Soybean	–	–	–	–	–	11	–	4	22	53	8	–	–	–	–
Sunflower	–	–	–	–	–	5	–	5	20	69	–	–	–	–	–
Sunflower, High Oleic	–	–	–	–	–	4	–	5	81	8	–	–	–	–	–
Palm	–	–	–	–	–	44	–	4	39	11	–	–	–	–	–
Cocoa Butter	–	–	–	–	–	26	–	34	35	3	–	–	–	–	–
Rapeseed *(B. campestris)*	–	–	–	–	–	4	–	2	33	18	9	–	12	–	22
Rapeseed *(B. napus)*	–	–	–	–	–	3	–	1	17	14	9	–	11	–	45
Mustard	–	–	–	–	–	4	–	–	22	24	14	–	12	–	20
Coconut	0.5	9	6.8	46.4	18	9	–	1	7.6	1.6	–	–	–	–	–
Palm Kernel	–	2.7	7.0	46.9	14.1	8.8	–	1.3	18.5	0.7	–	–	–	–	–
Jatropha curcas[2]	–	–	–	–	–	12.8	–	7.8	44.8	34	–	–	–	–	Other: 1.1
Pig	–	–	–	–	1	24	3	13	41	10	1	–	–	–	–
Beef	–	–	–	–	4	25	5	19	36	4	Trace	–	–	–	–
Sheep	–	–	–	–	3	21	2	25	34	5	3	–	–	–	–
Chicken	–	–	–	–	1	24	6	6	40	17	1	–	–	–	–
Turkey	–	–	–	–	1	20	6	6	38	24	2	–	–	–	–
Lard[3]	–	–	Trace	<0.5	1.5	24-30	2-3	12-18	36-52	10-12	1	0.5	0.5-1	–	<0.5
Beef Tallow[3]	–	–	–	Trace	2-4	23-29	2-4	20-35	26-45	2-6	1	<0.5	<0.5	Trace	Trace
Yellow Grease[4]	–	–	–	–	2.4	23.2	–	13.0	44.3	7.0	0.7	–	–	–	–

Yellow grease is a product from rendering plants, as well as waste oils and greases from restaurants. The fatty acid composition varies significantly depending on the source.

* The first number designates the number of carbon atoms and the second number designates the number of double bonds.

[1] Unless otherwise indicated, this information comes from: DeMan, John M.: "Principles of Food Chemistry (3rd Edition)," Springer – Verlag, http://www.knovel.com/knovel2/Toc.jsp?BookID=1093&VerticalID=0

[2] Shweta, Shah, Shweta, Sharma, and Gupta, M.N.: "Biodiesel Preparation by Lipase-Catalyzed Transesterification of Jatropha Oil," *Energy Fuels* 18, 1, 154-159, (2004).

[3] *Handbook of Indices of Food Quality and Authencity*, Singhai, R.S., Kulkarni, P.R., and Rege, D.V., Woodhead Publishing Limited, Abington Hall, Abington, Cambridge, CB1 6AH, England, (1997).

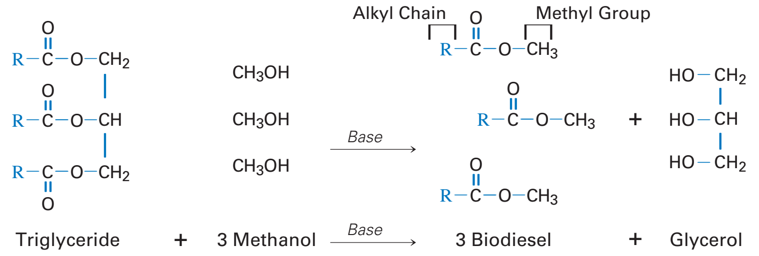
[4] *Organic Chemistry,* W.W. Lindstromberg, D.C. Health and Co., Lexington, MA, (1970).

In a process known as transesterification, triglycerides react in the presence of a base chemical (sodium or potassium hydroxide) with an alcohol, usually methanol, resulting in three fatty acids bonded to the methyl group from methanol (see Figure 4.5). These chemicals are referred to as fatty acid methyl esters (FAME) with alkyl chain lengths of 12 to 22 carbons. Water, base chemical, unreacted triglycerides and alcohol, and glycerin are byproducts of the transesterification reaction and must be removed from biodiesel fuel. The glycerin – also called glycerol – is purified and has uses in the cosmetic, food and other industries, and as an animal feed stock.[8, 9] Biodiesel has chemical and physical properties similar to those of conventional diesel fuel (see Table 4.7).

In the United States, soybean oil is the largest source of biodiesel, although oil from other plants is used as well. Canola oil (canola is a hybrid of rapeseed) is the source for most of the biodiesel produced in Europe. In countries where winters are warm, palm and coconut methyl esters are commonly used. Jatropha nut oil esters are becoming important in India and Africa, where the jatropha plant tolerates poor soil and is disease resistant.

Figure 4.5

Transesterification of Vegetable Oil to Biodiesel



R is typically 16 or 18 carbons and contains zero to three carbon-carbon double bonds.

Table 4.7

Comparison of Typical Properties of Biodiesel and Ultra-Low Sulfur Diesel (ULSD) Fuel

Property	Biodiesel	ULSD
Flash Point, °C	130	60
Cetane Number	55	44
Sulfur, ppm	<15	15
Relative Density, 15°C	0.88	0.85
Kinematic Viscosity at 40°C, mm^2/s	6.0	2.6
Heating Value, net, Btu/gal (kJ/kg)	128,000 (40,600)	130,000 (42,700)

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[8] Kinast, J.A.: "Production of Biodiesels from Multiple Feedstocks and Properties of Biodiesels and Biodiesel/Diesel Blends," final report, Report 1 in a series of 6, NREL/SR-510-31460 Gas Technology Institute Des Plaines, Illinois, National Renewable Energy Laboratory, U.S. Department of Energy, Golden, Colorado (March 2003).

[9] Knothe, Gerhard, Van Gerpen, Jon and Krahl, Jürgen, The Biodiesel Handbook, 2005, The American Oil Chemists' Society, www.aocs.org

ISSUES REGARDING THE USE OF BIODIESEL

The Engine Manufacturers Association (EMA) and a consortium of fuel injection equipment manufacturers recommend the use of biodiesel blends that contain no more than five percent by volume biodiesel (B5).[10] Higher concentrations such as B20 are not universally accepted, however, some OEM's have produced models that can run on B20. The general concern with higher-than-B5 is the lack of convincing data to ensure that use of such fuels does not lead to engine performance issues, such as filter plugging, injector coking, piston ring sticking and breaking, elastomer seal swelling and hardening/cracking, and engine lubricant degradation. At low ambient temperatures biodiesel becomes more viscous than diesel fuel, thus its use in colder climates is limited. As more research programs are done, and as more changes are made to the design of new engines, it is anticipated that more biodiesel will be produced and used. The new findings also will aid the industry to reach consensus to adopt fuel specifications at ASTM.

The U.S. Department of Energy (DOE) has warned consumers about the use of raw vegetable oils and animal fats. The DOE has stated that "Raw or refined vegetable oil, or recycled greases that have not been processed into biodiesel are not biodiesel and should be avoided."[11]

Limited testing has shown that biodiesel fuel produces lower emissions of particulate matter, hydrocarbons, and carbon monoxide than conventional diesel fuel; however, the same emissions reduction can also be achieved by installing a catalytic converter in the vehicle exhaust system. Early studies indicated that emissions of NO_x can be slightly higher than with conventional diesel, unless the fuel system injection timing is optimized for the fuel. Work is ongoing to determine the emissions from the use of biodiesel fuel.

The energy content of neat biodiesel is slightly lower than that of conventional diesel, but limited road testing has shown no appreciable loss in performance or mileage. Neat biodiesel has good lubricity properties and contains essentially no sulfur or aromatics. However, it has a relatively high pour point, which could limit its use in cold weather. Biodiesel fuels degrade more rapidly than conventional diesel fuel and this property may lead to increased biological growth during storage. Biodiesel is also more susceptible to oxidative degradation than petroleum diesel.

GAS-TO-LIQUID DIESEL

Another class of synthetic (non-crude oil derived) diesel fuel that has received significant attention recently is referred to as gas-to-liquid (GTL) diesel. GTL diesel is produced from

[10] "Technical Statement on the Use of Biodiesel Fuel in Compression Ignition Engines," Engine Manufacturers Association, http://www.enginemanufacturers.org/admin/library/upload/297.pdf

[11] "Biodiesel Handling and Use Guidelines, Second Edition," DOE/GO-102006-2288, National Renewable Energy Laboratory, U.S. Department of Energy, (01 March 2006).

natural gas using the Fischer-Tropsch® process, which was first developed in the 1920s. The Fischer-Tropsch® process uses special catalysts to convert natural gas through a carbon monoxide-hydrogen intermediate into a mixture of synthetic hydrocarbons referred to as syncrude. The syncrude is further refined via isomerization, hydrocracking/hydrotreating, and fractionation processes to produce a completed fuel.

GTL processes can yield high-quality fuels with exceptional properties. Refined syncrude diesel, GTL diesel, is composed almost exclusively of paraffins, with virtually no aromatic hydrocarbon or olefins content. In addition, GTL diesel fuel is nearly free of sulfur and nitrogen. The cetane number of GTL diesel is significantly higher than conventional diesel – typically in the range from 70 to 75. GTL diesel is characterized by poor lubricity and must be treated with a commercial lubricity additive. In addition, it also has poor cold flow properties, limiting its potential use in cold weather applications.

At the same time, properly treated GTL diesel is fully compatible with existing diesel engine technology and can be used interchangeably (and mixed) with conventional diesel fuel. The energy density of GTL diesel is similar to conventional diesel. Typically, GTL diesel results in lower hydrocarbon, carbon monoxide, nitrogen oxide, and particulate emissions when compared with conventional diesel fuel. GTL diesel does not provide any advantage, however, in terms of CO_2 tailpipe emissions.

GTL diesel has not seen widespread commercial use. Its intrinsic advantage of upgrading low-grade natural gas to valuable liquid products is balanced against capital investment and production costs, which are significantly higher for GTL fuels than for its crude-dervied counterparts. However, over the past decade, technological advances have been made that significantly reduce the cost of producing GTL fuels. As GTL production technology continues to improve and global energy demand continues to increase, GTL fuels will become increasingly cost competitive and will become more common in the marketplace.

OTHER DIESEL FUEL PRODUCTS

Ethanol in diesel emulsions (E diesel) and water-in-diesel emulsions are examples of products people have investigated because they reduce tailpipe emissions of the criteria pollutants. (See *Chapter 3 – Diesel Fuel and Air Quality*.) However, many of the properties of E diesel are lower than specified in ASTM D 975: flash point (E diesel needs to be treated as a Flammability Class I liquid,) cetane number, and viscosity; heat content is also lower than in conventional diesel fuel. Both of these emulsions require the addition of large concentrations of additives to stabilize the emulsion. However, with the combination of new engine designs (see *Chapter 6 – Diesel Engines*) and exhaust after-treatment devices, using 15 ppm sulfur diesel fuel does a better job of reducing tailpipe emissions. (See *Chapter 3 – Diesel Fuel and Air Quality*.)

5 • Diesel Fuel and Biodiesel Fuel Specifications and Test Methods

It has been critical to the successful development of diesel fuel and diesel-powered vehicles to have consensus among refiners, vehicle and engine manufacturers, and other interested parties on the characteristics of diesel fuel necessary for satisfactory performance and reliable operation. In the United States, this consensus is reached under the auspices of ASTM International (formerly American Society for Testing and Materials. The name was changed to ASTM International to reflect the fact that many of the specifications are used in other parts of the world.) The European Union has also developed specifications for diesel fuels. These specifications are used extensively in Asia and the Pacific basin countries, with modifications to fit local supply, crudes, and regulations.

ASTM International is an organization of committees. Committee D-2 (*Petroleum Products and Lubricants*) is responsible for diesel fuel specifications and test methods. The committee members bring to the D-2 forum the viewpoints of groups interested in and affected by diesel fuel specifications. These groups include:

- Vehicle and engine manufacturers
- Refiners
- Petroleum marketing organizations
- Additive suppliers
- Governmental regulatory agencies (such as the EPA and state regulatory agencies)
- General interest groups, consumer groups, and consultants

Committee D-2 can also turn to groups, such as the SAE International (formerly the Society of Automotive Engineers) and the Coordinating Research Council (CRC), for additional reliable technical data to help establish a specification or develop a test method.

Table 5.1 lists a number of important diesel fuel properties and indicates how they affect performance. The table also notes whether the property is determined by the bulk composition of the fuel or by the presence or absence of minor components. Also in the table is a column noting the time frame of the performance effect – whether it typically occurs immediately or after hundreds of hours of operation (long-term).

SPECIFICATIONS – ASTM INTERNATIONAL

Many of the properties in Table 5.1 are addressed by ASTM D 975 – *Standard Specification for Diesel Fuel Oils*, which covers seven grades of diesel fuel oil suitable for various types of diesel engines.

Table 5.1

Relationship of Diesel Fuel Properties to Composition and Performance Property

Property	Property Type*	Effect of Property on Performance	Time Frame of Effect
Flash Point	Minor	Safety in handling and use – not directly related to engine performance	–
Water and Sediment	Minor	Affect fuel filters and injectors	Long-term
Volatility	Bulk	Affects ease of starting and smoke	Immediate
Viscosity	Bulk	Affects fuel spray atomization and fuel system lubrication. It also affects fuel system leakage.	Immediate and Long-term
Ash	Minor	Can damage fuel injection system and cause combustion chamber deposits	Long-term
Sulfur	Minor	Affects particulate emissions, cylinder wear, and deposits	Particulates: Immediate Wear: Long-term
Copper Strip Corrosion	Minor	Indicates potential for corrosive attack on metal parts	Long-term
Cetane Number	Bulk	Measure of ignition quality – affects cold starting, smoke, combustion, and emissions	Immediate
Cloud Point and Pour Point	Minor	Affect low-temperature operability and fuel handling	Immediate
Carbon Residue	Minor	Measures coking tendency of fuel; may relate to engine deposits	Long-term
Heating Value (Energy Content)	Bulk	Affects fuel economy	Immediate
Density	Bulk	Affects heating value	Immediate
Stability	Minor	Indicates potential to form insoluble particles and gum/residues in the fuel during use and/or in storage	Immediate and Long-term
Lubricity	Minor	Affects fuel injection system (pump and injector) wear	Moderate: Long-term Severe: Short-term
Water Separability	Minor	Affects ability of water to separate from the fuel	Immediate and Long-term
Low-Temperature Operability	Bulk	Affects flow and filterability at cold ambient temperatures	Immediate

* A bulk property is one that is determined by the composition of the fuel as a whole. A minor property is one that is determined by the presence or absence of minor components.

Table 5.2

ASTM D 975 Requirements for Diesel Fuel Oils

Property	Test Method	S15, S500, S5000* No. 1-D	S15, S500, S5000* No. 2-D	No. 4-D
Flash Point, °C (°F), min	D 93	38 (100)	52 (125)	55 (130)
Water and Sediment, % volume, max	D 2709	0.05	0.05	–
	D 1796			0.50
Distillation Temperature, °C (°F), 90% Volume Recovered:	D 86			
min			282 (540)	
max		288 (550)	338 (640)	
Or				
Simulated Distillation, °C (°F) (Does not apply to No. 1-D S5000 or No. 2-D S15) 90% Volume Recovered:	D 2887			
min		304 (572)	300 (572)	
max			356 (673)	
Kinematic Viscosity, mm^2/sec at 40°C (104°F):	D 445			
min		1.3	1.9	5.5
max		2.4	4.1	24.0
Ash, % mass, max	D 482	0.01	0.01	0.10
Sulfur, ppm (µg/g), max	D 5453	15	15	–
% mass, max	D 2622	0.05	0.05	–
% mass, max	D 129	0.50	0.50	2.00
Copper Strip Corrosion Rating, max After 3 hours at 50°C (122°F)	D 130	No. 3	No. 3	–
Cetane Number, min	D 613	40	40	30
One of the following must be met:				
(1) Cetane Index, min	D 976-80	40	40	–
(2) Aromaticity, % volume, max	D 1319	35	35	–
Cloud Point, °C (°F), max	D 2500	Varies	Varies	–
Or				
LTFT/CFPP, °C (°F), max	D 4539/ D 6371			
Ramsbottom Carbon Residue, max (% mass on 10% Distillation Residue)	D 524	0.15	0.35	–
Lubricity, 60°C, WSD, microns, max	D 6079	520	520	--

* The fuel grades S15, S500, and S5000 refer to the maximum sulfur content allowed in the fuel expressed in ppm by weight (e.g., S15 refers to diesel fuel with a maximum sulfur content of 15 ppm).

The specification prescribes the required properties of diesel fuel and sets the limits (requirements) for the values of these properties. These requirements are listed in Table 5.2 for the seven grades of diesel fuel defined by the specification. Specification D 975 also contains the standard test methods used to measure the values of the properties. These methods are described in the *Test Methods* section at the end of this chapter.

The D 975 specification contains the minimum mandatory requirements needed to guarantee acceptable performance for the majority of users. In addition, this specification recognizes some requirements established by the EPA to reduce emissions. For a variety of reasons, other organizations may establish additional requirements, such as:

- **State governments:** To reduce emissions, CARB, for example, established additional requirements for vehicular diesel fuel, which became effective in 1993.
- **Pipelines:** Some companies that transport diesel fuel have limits for density and pour point, properties that ASTM D 975 does not limit.
- **Some purchasers:** Beyond these minimum requirements, any fuel users, especially private or government fleets using large volumes of diesel fuel, can specify additional requirements by contract, if it is mutually acceptable to the purchaser and the supplier. A fuel supplier must ensure that its diesel meets all these requirements, not just those of ASTM D 975.

There are ongoing discussions within industry groups to create fuel specifications that meet the needs of new engine technologies and fuel formulations. Existing specifications can be changed and new properties can be adopted to meet these needs. For example, the Engine Manufacturers Association (EMA) has proposed raising the minimum cetane number if results from engine testing warrant the change.

With the North American introduction of S15 diesel fuel, conductivity is of concern to some. Species that promote conductivity are removed by the hydrotreating required to reduce sulfur to 15 ppm. Lower sulfur fuels tend to have lower conductivity. Additives known as Static Dissipator Additives can be added to fuels to increase the conductivity, thus dissipating static charge. A conductivity requirement is being added to ASTM D 975 (see side bar).

CONDUCTIVITY

Conductivity of a fuel is a measure of its ability to dissipate static electric charge. It is expressed in pS/m, picosiemens-per-meter, also called a conductivity unit (CU). A siemen is the SI (metric) definition of reciprocal ohm, sometimes called mho.

$1\ pS/m = 1 * 10^{-12}\ \Omega^{-1}\ m^{-1}$
$= 1\ CU$
$= 1\ picomho/m$

SPECIFICATIONS – THE EUROPEAN UNION

Diesel fuel specifications in the European Union are similar, but not identical, to those in the U.S. For example, the minimum cetane number in Europe is higher and there is a density range requirement. The automotive fuel standards are developed by the European Standards Organization (CEN); the most recent specification for diesel fuel is in Table 5.3.

Table 5.3

EN 590 Diesel Fuel Requirements and Test Methods – Date Introduced: 1/1/2005

Diesel Specification Parameter	Units	Limits	Test Method
Cetane Number		51.0 minimum	EN ISO 5165
Cetane Index		46.0 minimum	EN ISO 4264
Density at 15°C	kg/m^3	820 minimum to 845 maximum	EN ISO 3675 EN ISO 12185
Polycyclic Aromatic Hydrocarbons	% (m/m)	11 maximum	EN 12916
Sulfur Content	mg/kg	50.0 maximum 10.0 maximum	EN ISO 20846 EN ISO 20847 EN ISO 20884
Flash Point	°C	>55	EN ISO 2719
Carbon Residue (on 10% Dist. Residue)	% (m/m)	0.30 maximum	EN ISO 10370
Ash Content	% (m/m)	0.01 maximum	EN ISO 6245
Water Content	mg/kg	200 maximum	EN ISO 12937
Total Contamination	mg/kg	24 maximum	EN 12662
Copper Strip Corrosion (3 Hours at 50°C)		class 1	EN ISO 2160
Oxidation Stability	g/m^3	25 maximum	EN ISO 12205
Lubricity, WSD at 60°C	µm	460 maximum	EN ISO 12156-1
Viscosity at 40°C	mm^2/sec	2.00 minimum to 4.50 maximum	EN ISO 3104
Distillation			EN ISO 3405
Vol. Recovered at:			
250°C	% (V/V)	<65	
350°C	% (V/V)	85 minimum	
95% Point	°C	360 maximum	
Fatty Acid Methyl Esters (FAME) Content	% V/V	5 maximum	EN 14078

Canada

Specifications for diesel fuel quality in Canada are the responsibility of the Middle Distillates Committee of the Canadian General Standards Board. The six standards for diesel fuel depend upon the application in general areas of automotive, mining, locomotive, and naval, with several types of diesel fuel covered by each standard.

Canadian sulfur concentration requirements generally align with those of the U.S. EPA:

- Sulfur in on-road diesel is 15 ppm
- Sulfur in off-road diesel will be 500 ppm in 2007, then drop to 15 ppm in 2010
- Sulfur in locomotive and marine diesel fuels must be 500 ppm sulfur by 2007 and 15 ppm by 2012

Japan

The quality of diesel fuel in Japan is specified by the Japanese Industrial Standard, JIS K 2204. There are five grades of diesel fuel – Special No. 1, No. 1, No. 2, No. 3, and Special No. 3 – with cetane number ranging from 50 to 45 and T90 distillation temperature from 360°C to 330°C. Before 2007, the sulfur content limit in JIS K 2204 diesel fuels in Japan is 50 ppm; in 2007, the 10 ppm sulfur limit becomes effective.

Highway vehicles (passenger cars, trucks, and buses) normally use No. 2 diesel fuel. Special No. 3 diesel is used as the winter grade in Hokkaido and other cold climate areas. Most Japanese off-road equipment also uses No. 2 diesel fuel grade, with some of them using fuel oil equivalent to No. 1 of Category I specified by JIS K 2205 (sulfur limit in the latter remains at 0.5 percent).

Other Countries

In general, the emissions and fuel standards of other countries are based on European, Japanese, or U.S. regulations. For example, Australian emission standards are based on European regulations with certain U.S. and Japanese standards accepted for selected applications. The long-term policy is to fully harmonize Australian regulations with European standards. Brazilian standards are primarily based on European regulations, while Singapore adopts a mixture of regulations from the U.S., Europe, and Japan.

PREMIUM DIESEL

In recent years, environmental regulations have significantly affected diesel fuel formulation and specification limits. The introduction of tighter limits, coupled with rapid changes in engine design to meet new emission regulations, created the need to address several fuel properties to ensure proper performance while minimizing engine maintenance problems.

Some fuel users believe that, under certain circumstances, they can benefit from diesel fuel with properties modified beyond the minimum ASTM D 975 specifications. A number of fuel suppliers offer these specially formulated fuels in addition to normal diesel fuel. Diesel fuel with these modifications is often called *premium diesel*, although other names are also used.

The premium diesel concept differs from that of premium gasoline. Gasoline engines of certain types and compression ratios require a higher octane number fuel to avoid knocking. Therefore, all fuel suppliers offer a higher octane level of premium gasoline for these vehicles.

Conversely, premium diesel is typically related to varying multiple fuel properties. Some of the more commonly modified fuel properties are: cetane number, low-temperature operability, stability, lubricity, detergency, and heating value. The premium diesel fuel suppliers tailor the specific properties of their premium diesel to match the various performance demands in different marketing regions. The level of improvement in each property usually varies from one supplier to another and may also vary from region to region.

Several organizations have proposed meaningful standards for premium diesel. The intent of these standards is to ensure that all diesel fuel carrying the “premium” classification provides significant functional benefits when compared to normal diesel fuel. Currently, the National Conference on Weights and Measures (NCWM), the Engine Manufacturers’ Association (EMA), and the Alliance of Automobile Manufacturers (AAM) have made the three most complete proposals. The NCWM’s premium diesel proposal has received the most widespread support to date.

National Conference on Weights and Measures

The NCWM, a national organization based in the U.S., is composed of a board of directors, four standing committees, four regional associations, and state organizations that develop and propose national model laws and regulations for products sold in the United States. As with ASTM International, the standards developed by NCWM carry no inherent legal authority; their standards become law only after they are officially adopted by the relevant federal, state, or local governmental authorities.

The NCWM Premium Diesel Working Group responsible for defining premium diesel is composed of representatives from the oil industry, engine manufacturers, additive manufacturers, independent labs, and government agencies. This group is guided by two principles: functionality and practicality. A premium fuel property must be one that, when enhanced from its average value in conventional diesel, provides a *functional* benefit to consumers – a benefit that has been technically demonstrated. There must also be a *practical* means of enforcing the enhanced value – it must be measurable by a recognized test method accepted by the industry. The current NCWM premium diesel fuel definition sets property specifications for cetane number, low-temperature operability, thermal stability and lubricity as shown in Table 5.4.

Table 5.4
NCWM Premium Diesel Property Requirements

Fuel Property	Test Method	NCWM Premium Diesel Recommendation
Cetane Number, min	ASTM D 613	47.0
Low-Temperature Operability	ASTM D 2500 or ASTM D 4539	ASTM D 975 Tenth percentile minimum ambient air temperature
Thermal Stability, 180 minutes 150°C, % Reflectance, min	ASTM D 6468	80%
Lubricity, 60°C, WSD, microns, max*	ASTM D 6079	520

* ASTM D 975 adopted the same lubricity requirement starting January 2005. Currently, the NCWM lubricity requirement states that if a single test result is more than 560 microns, a second test shall be conducted. The average of the two values can not be greater than 560 microns.

BIODIESEL FUEL STANDARDS

ASTM International Biodiesel Blend Stock Standard

In 2003, the ASTM International approved ASTM D 6751, the standard specification for biodiesel blend stock (B100) for middle distillate fuels. The specification covers biodiesel (B100) Grades S15 and S500 for use as a blend component with petroleum diesel fuel oils as defined by specification D 975 Grades 1-D, 2-D, and low sulfur 1-D and 2-D. Table 5.5 shows the requirements for biodiesel (B100) blend stock.

Table 5.5

ASTM D 6751 Detailed Requirements for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels

Property	Test Methods	Grade S15	Grade S500
Calcium and Magnesium, Combined, ppm (µg/g), max	EN 14538	5	5
Flash Point (Closed Cup), °C (°F), min	D 93	93 (199)	93 (199)
Alcohol Content One of the following must be met: 1. Methanol content, max 2. Flash point, min	 EN 14110 D 93	 0.2 130	 0.2 130
Water and Sediment, % vol, max	D 2709	0.050	0.050
Kinematic Viscosity, 40°C (104°F), mm^2/sec	D 445	1.9 - 6.0	1.9 - 6.0
Sulfated Ash, % mass, max	D 874	0.020	0.020
Sulfur, % mass (ppm), max	D 5453	0.0015 (15)	0.05 (500)
Copper Strip Corrosion, max	D 130	No. 3	No. 3
Cetane Number, min	D 613	47	47
Cloud Point, °C	D 2500	Report	Report
Carbon Residue, % mass, max	D 4530	0.050	0.050
Acid Number, mg KOH/g, max	D 664	0.50	0.50
Free Glycerin, % mass	D 6584	0.020	0.020
Total Glycerin, % mass	D 6584	0.240	0.240
Phosphorous Content, % mass, max	D 4951	0.001	0.001
Distillation Temperature, Atmospheric Equivalent Temperature, 90% Recovered, °C (°F), max	D 1160	360 (680)	360 (680)
Sodium and Potassium, Combined, ppm (µg/g), max	EN 14538	5	5
Oxidation Stability, hours, min	EN 14112	3	3

European Biodiesel Fuel and Blend Stock Standard

The European standard (EN 14214) specifies requirements for fatty acid methyl esters (FAME) to be used at 100 percent concentration or as a fuel extender for use in diesel engines in accordance with EN 590 (diesel fuel standard). Those requirements are shown in Table 5.6.

Table 5.6

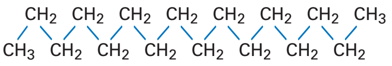
EN 14214 (E) Automotive Fuels – Fatty Acid Methyl Esters (FAME) for Diesel Engines – Requirements and Test Methods

Property	Test Methods	Limits
Ester Content, % (m/m), min	EN 14103	96.5
Density at 15°C, kg/m^3	EN ISO 3675 EN ISO 12185	860 to 900
Viscosity, 40°C (104°F), mm^2/sec	EN ISO 3104	3.5 to 5.0
Flash Point (Closed Cup), °C (°F), min	prEN ISO 3679	120.0 (248)
Sulfur, mg/kg, max	prEN ISO 20846 prEN ISO 20884	10
Carbon Residue (on 10% Distillation Residue), % m/m, max	EN ISO 10370	0.30
Cetane Number, min	EN ISO 5165	51.0
Sulfated Ash, % m/m, max	ISO 3987	0.02
Water, mg/kg, max	EN ISO 12937	500
Total Contamination, mg/kg, max	EN 12662	24
Copper Strip Corrosion, 3 Hours @ 50°C (122°F)	EN ISO 2106	Class 1
Oxidation Stability, 110°C (230°F), hours, min	EN 14112	6.0
Acid Value, mg KOH/g, max	EN 14104	0.50
Iodine Value, gr iodine/100 gr, max	EN 14111	120
Linolenic Acid Methyl Ester, % m/m, max	EN 14103	12.0
Polyunsaturated (≥ 4 Double Bonds) Methyl Esters, % m/m, max	–	1
Methanol Content, % m/m, max	EN 14110	0.20
Monoglyceride, % m/m, max	EN 14105	0.80
Diglyceride, % m/m, max	EN 14105	0.20
Triglyceride, % m/m, max	EN 14105	0.20
Free Glycerol, %m/m, max	EN 14105 EN 14106	0.02
Total Glycerol, % mass	EN 14105	0.25
Group I Metals, (Na + K) mg/kg, max	EN 14108 EN 14109	5.0
Group II Metals, (Ca + Mg) mg/kg, max	prEN 14538	5.0
Phosphorous Content, mg/kg, max	EN 14107	10.0

CETANE NUMBER AND OCTANE NUMBER

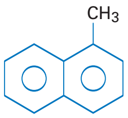
Cetane number (diesel fuel) and octane number (gasoline) both measure the tendency of the fuel to ignite spontaneously. In the cetane number scale, high values represent fuels that readily ignite and, therefore, perform better in a diesel engine. In the octane number scale, high values represent fuels that resist spontaneous ignition and, therefore, have less tendency to knock in a gasoline engine. Because both scales were developed so that the higher numbers represent higher quality for the respective use, high cetane number fuels have low octane numbers and vice versa.

n-Hexadecane



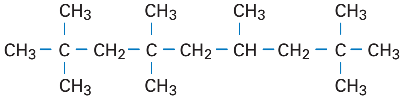
Hexadecane (cetane), cetane number = 100

1-Methylnaphthalene



1-Methylnaphthalene, cetane number = 0

Heptamethylnonane



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

2,2,4,4,6,8,8-Heptamethylnonane (Isocetane)
cetane number = 15

TEST METHODS

ASTM International will not adopt a requirement for a property until a standard test method is developed to measure that property. The test method development process starts with a technical review of the proposed method. Next, an inter-laboratory test protocol (round robin) is conducted on a common set of samples sent to a group of labs, which independently analyze them. The results from the participating laboratories are compiled and statistically reviewed. If the agreement among labs is acceptable, a precision statement is developed that contains the maximum difference to be expected between back-to-back tests in one laboratory (repeatability) and the maximum difference between results obtained by different laboratories on the same sample (reproducibility).

Many of the ASTM International test methods were developed from the 1920s through the 1940s; however, test methods based on new technology are continually being adopted. To ensure that they remain up to date, ASTM International requires the review of each test method every five years for re-approval, revision, or cancellation.

The year of last review appears after the hyphen in each test method number. For example, ASTM D 86-05 – *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure*, originally published as a tentative method in 1921, was last reviewed in 2005.

D 975 Specific Test Methods

Cetane Number

ASTM D 613 – *Standard Test Method for Cetane Number of Diesel Fuel Oil*

This test method for diesel fuel was developed in the 1930s by the Cooperative Fuel Research (CFR) committee and later standardized by ASTM. The method involves running the fuel in a single-cylinder engine with a continuously variable compression ratio under a fixed set of conditions. Although the method has been updated over the years, it is still based on the original engine design.

Two specific hydrocarbons were originally chosen to define the cetane number scale:

- 1-methylnaphthalene (also called α*-methylnaphthalene*), which burns poorly in a diesel engine, was assigned a cetane number of zero.
- n-hexadecane (cetane), which burns well, was assigned a cetane number of 100.

These hydrocarbons are the *primary reference fuels* for the method.

The cetane number of a fuel was originally defined as the volume percent of n-hexadecane in a blend of n-hexadecane and 1-methylnaphthalene that gives the same ignition delay period as the test sample. For example, a fuel with a cetane number of 40 will perform the same in the engine as a blend of 40 percent n-hexadecane and 60 percent 1-methylnaphthalene.

In 1962, the low-cetane number primary reference fuel was replaced with 2,2,4,4,6,8,8-heptamethylnonane (sometimes called isocetane). The change was made because 1-methylnaphthalene had been found to be somewhat unstable, expensive, and difficult to use in the CFR engine. When measured against the two original primary standards, 2,2,4,4,6,8,8-heptamethylnonane has a cetane number of 15. When the low-cetane number primary reference fuel was changed, the equation used to calculate cetane number was modified to keep the cetane number scale the same.

In day-to-day operations, two secondary reference fuels replace the two primary reference fuels. These fuels are periodically prepared in large volume and made available to testing labs. Their cetane numbers are determined by calibrating them against the primary reference fuels. The work is done by the many labs that are members of the ASTM International Diesel National Exchange Group.

Cetane number can be determined by other methods such as the Ignition Quality Tester (IQT). ASTM D 6890 – *Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber* describes this test method. This method measures ignition delay and uses a constant volume combustion chamber with direct fuel injection into heated, compressed air. An equation is used to convert an ignition delay determination to a derived cetane number (DCN).

Diesel specification ASTM D 975 allows the use of the IQT as an alternate method to ASTM D 613, which remains as the referee test method.

Calculated Cetane Index

ASTM D 976 – *Calculated Cetane Index of Distillate Fuels*
ASTM D 4737 – *Calculated Cetane Index by Four-Variable Equation*

Because measuring the cetane number requires acquiring and maintaining a cetane number engine, it is apparent that it is a difficult and expensive test. There have been many attempts to develop methods to estimate the cetane number of a fuel for situations where an engine is not available or the amount of fuel is insufficient for the engine test. To differentiate them from the engine test, these estimates are known as Calculated Cetane Indexes.

ASTM D 976 uses the density of the fuel and its mid-distillation temperature to estimate the cetane number. An improved method, ASTM D 4737, uses the density of the fuel and the distillation temperatures at 10 percent volume, 50 percent volume, and 90 percent volume recovery to estimate the cetane number. There are other calculated cetane index methods based on other physical, chromatographic, or spectroscopic properties of the fuel, but they are not widely used.

A calculated cetane index estimates the "natural" cetane number of the fuel. Because the calculations involve bulk fuel properties, this index is not affected by the presence of cetane number improvers (diesel ignition improvers). These additives increase the cetane number of a fuel, but do not change its calculated cetane index.

ASTM D 4737 includes two procedures for estimating the cetane number:

- Procedure A – Developed for diesel fuels meeting the requirements of Specification D 975 Grade 1-D S500 and Grades 1-D, 2-D, and 4-D S5000
- Procedure B – Developed for diesel fuels meeting the requirements of Specification D 975 Grade 2-D S500

Each of these procedures is shown in the list of test methods, under ASTM D 4737 *Calculated Cetane Index by Four Variable Equation*. Data are being generated to evaluate the correlation with S15.

Low-Temperature Operability

Institute of Petroleum (IP) 309 – *Cold Filter Plugging Point of Distillate Fuels (CFPP)*
ASTM D 6371 – *Cold Filter Plugging Point of Diesel and Heating Fuels*
ASTM D 4539 – *Filterability of Diesel Fuels by Low-Temperature Flow Test (LTFT)*

Sometimes a combination of fuel behavior and fuel system design can cause filter plugging. While some fuel systems plug at the cloud point temperature, many others can operate several degrees below the cloud point. This happens because low-temperature filterability depends on the size and shape of wax crystals, not merely on their presence.

Considerable effort has been made to develop a laboratory test that correlates with field performance, especially for additized fuels. This effort focused on dynamic tests that simulate flow through a filter in the fuel system, rather than on static physical property tests.

One dynamic test that is widely accepted in Europe is the CFPP (Institute of Petroleum test method 309/EN 116). ASTM D 6371 is a similar method. In this test, the sample is cooled by immersion in a constant temperature bath. The cooling rate is non-linear and fairly rapid – about 40°C/hour. The CFPP is the temperature of the sample when 20 ml of the fuel fails to pass through a wire mesh in less than 60 seconds. CFPP appears to over estimate the benefit obtained from the use of certain additives, especially for North American vehicles.

ASTM D 4539 – *Low-Temperature Flow Test (LTFT)* is a similar dynamic test developed in the U.S. In contrast to CFPP, LTFT uses a slow constant cooling rate of 1°C/hour. This rate mimics the temperature behavior of fuel in the tank of a diesel truck left overnight in a cold environment with its engine turned off. LTFT also correlates well with low-temperature operability field tests. However, because of the slow cooling rate, LTFT requires 12 to 24 hours to complete, making it impractical to use for routine fuel testing.

While ASTM D 975 does not include a low-temperature operability requirement, it offers a guideline: "field work suggests that cloud point (or wax appearance point) is a fair indication of the low-temperature operability limit of fuels without cold flow additives in most vehicles."

Lubricity

ASTM D 6078 – *Scuffing Load Ball-On-Cylinder Lubricity Evaluator (SLBOCLE)*
ASTM D 6079 – *High-Frequency Reciprocating Rig (HFRR)*

There is no doubt that lubricity is an important property of diesel fuel performance. A single tankful of fuel with extremely low lubricity can cause fuel injection system components, such as a fuel pump, to catastrophically fail. Setting a lubricity requirement to prevent catastrophic failure is relatively easy; setting a requirement to avoid long-term fuel system wear is much harder.

There are three ways to evaluate the lubricity of a fuel. In order of decreasing long-term and increasing simplicity, they are:

- Vehicle testing
- Fuel injection equipment bench tests
- Laboratory lubricity testing

Vehicle tests require a lot of fuel, time, and effort. They are usually reserved for basic studies of fuel performance. Fuel injection equipment bench tests, such as ASTM D 6898, require 50 to 100 gallons samples of fuel and 500 to 1,000 hours of operating time. Both ASTM D 6078 and D 6079 are relatively quick, inexpensive, and easy to perform.

HFRR has become the dominant test method for fuels specification. In the United States, ASTM D 975 – *Standard Specification for Diesel Fuel Oils* requires that all grades of fuel, Grade 1-D and Grade 2-D, at all sulfur levels have wear scar diameters no larger than 520 microns using the HFRR at 60°C. Europe and many regions in Asia Pacific have adopted a more stringent maximum wear scar diameter of 460 microns maximum.

A lot of work has been done in the past few years to correlate these laboratory tests with field performance. Some SLBOCLE studies indicate that fuels with values below 2,000 gram (g) will usually cause accelerated wear in rotary-type fuel injection pumps. Fuels with values above 2,800 g will usually perform satisfactorily.

The HFRR and the SLBOCLE tests can indicate that fuels treated with an effective lubricity additive have poor lubricity, while the more accurate fuel injection equipment bench test rates them acceptable.

Table 5.7 contains a list of the test methods approved for determining diesel fuel properties.

Table 5.7
Diesel Fuel Test Methods

Property	Standard Test Method	Description
Flash Point	ASTM D 93 – *Flash-Point by Pensky-Martens Closed Cup Tester (IP 34)*	At least 75 milliliters are required for this test. The sample is stirred and heated at a slow, constant rate in a closed cup. The cup is opened at intervals, and an ignition source is moved over the top of the cup. The flash point is the lowest temperature at which the application of the ignition source causes the vapors above the liquid to ignite.
Water and Sediment	ASTM D 2709 – *Water and Sediment in Middle Distillate Fuels by Centrifuge*	Water and sediment are fuel contaminants. In this test, a 100-milliliter sample is centrifuged under specified conditions in a calibrated tube. The amount of sediment and water that settles to the bottom of the tube is read directly using the scale on the tube.
Distillation	ASTM D 86 – *Distillation of Petroleum Products*	The distillation profile is a fundamental fuel property. In this test, a 100-milliliter sample is placed in a round-bottom flask and heated to obtain a controlled rate of evaporation. The temperature is recorded when the first drop is collected (the initial boiling point), at recovered volume percentages of 5 percent, 10 percent, every subsequent 10 percent to 90 percent, 95 percent, and at the end of the test (end point/final boiling point).
	ASTM D 2887 – *Boiling Range Distribution of Petroleum Fractions by Gas Chromatography (IP 406)*	This test can be used as an alternate to ASTM D 86 with the limits listed in Table 1 of ASTM D 975. The boiling range distribution determination by distillation is simulated by the use of gas chromatography. A non-polar packed or open tubular (capillary) gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point. The column temperature is raised at a reproducible linear rate and the area under the chromatogram is recorded throughout the analysis. Boiling points are assigned to the time axis from a calibration curve obtained under the same chromatographic conditions by analyzing a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling range distribution can be obtained.

Property	**Standard Test Method**	**Description**
Viscosity	ASTM D 445 – *Kinematic Viscosity of Transparent and Opaque Liquids (IP 71)*	The sample is placed in a calibrated capillary glass viscometer tube and held at a closely controlled temperature. The time required for a specific volume of the sample to flow through the capillary under gravity is measured. This time is proportional to the kinematic viscosity of the sample.
Ash	ASTM D 482 – *Ash from Petroleum Products (IP 4)*	The sample is placed in a crucible, ignited, and allowed to burn. The carbonaceous residue is heated further in a muffle furnace to convert all the carbon to carbon dioxide and all the mineral salts to oxides (ash). The ash is then cooled and weighed.
Sulfur	ASTM D 5453 – *Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence*	**This method is applicable to all grades and is the referee method for all S15 grades.** Up to 20 µL of the sample (sample size is based on estimated sulfur concentration) is injected into a high-temperature combustion tube where the sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen-rich atmosphere. Water produced during the sample combustion is removed and the sample combustion gases are then exposed to ultraviolet (UV) light. The SO_2 absorbs the energy from the UV light and converts it to excited sulfur dioxide (SO_2^*). The fluorescence emitted from the excited SO_2^* as it returns to a stable state, SO_2, is detected by a photomultiplier tube, and the resulting signal is a measure of the sulfur contained in the sample.
	ASTM D 2622 – *Sulfur in Petroleum Products by X-Ray Spectrometry*	**This is the referee method for all S500 grades.** The sample is placed in an x-ray beam and the intensity of the sulfur x-ray fluorescence is measured. This method is not recommended for determining the sulfur concentration of S15 diesel fuel because the repeatability is poor.

Property	Standard Test Method	Description
Sulfur	ASTM D 129 – *Sulfur in Petroleum Products (General Bomb Method) (IP 61)*	**This is the referee method for No. 1-D and No. 2-D S5000 and No. 4-D.** This test method covers the determination of sulfur in petroleum products, including lubricating oils containing additives, additive concentrates, and lubricating greases that cannot be burned completely in a wick lamp. The test method is applicable to any petroleum product sufficiently low in volatility that can be weighed accurately in an open sample boat and contains at least 0.1 percent sulfur.
	ASTM D 7039 – *Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry*	NOTE: At the time of this publication, this method has been proposed for addition to D 975. This test method covers the determination of total sulfur by monochromatic, wavelength-dispersive X-ray fluorescence (MWDXRF) spectrometry in single-phase gasolines, diesel fuels, and refinery process streams used to blend gasoline and diesel, at sulfur concentrations from 2 to 500 mg/kg.
Copper Strip Corrosion	ASTM D 130 – *Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test (IP 154)*	A polished copper strip is immersed in the sample for three hours at 50°C (122°F) and then removed and washed. The condition of the copper surface is qualitatively rated by comparing it to standards.
Cetane Number	ASTM D 613 – *Cetane Number of Diesel Fuel Oil (IP 41)*	The cetane number of a diesel fuel oil is determined by comparing its combustion characteristics in a test engine with those for blends of reference fuels of known cetane number under standard operating conditions. This is accomplished using the bracketing handwheel procedure. This procedure varies the compression ratio (handwheel reading) for the sample and each of two bracketing reference fuels to obtain a specific ignition delay permitting interpolation of cetane number in terms of handwheel reading.

Property	Standard Test Method	Description
Calculated Cetane Index	ASTM D 4737 – *Calculated Cetane Index by Four Variable Equations*	ASTM D 4737 provides a means for estimating the ASTM cetane number (Test Method D 613) of distillate fuels from density and distillation recovery temperature measurements. Two correlations in SI units have been established between the ASTM cetane number and the density and 10 percent, 50 percent, and 90 percent distillation recovery temperatures of the fuel. Use Procedure A for Grades No. 1–D S500, No. 1–D S5000, No. 2–D S5000, and No. 4–D S5000. **Procedure A** $\mathrm{CCI} = 45.2 + (0.0892)\,[T_{10N}] + [0.131 + (0.901)\,(B)]\,[T_{50N}] + [0.0523 - (0.420)\,(B)]\,[T_{90N}] + [0.00049]\,[(T_{10N})^2 - (T_{90N})^2] + (107)\,(B) + (60)\,(B)^2$ Where: CCI = Calculated Cetane Index by Four Variable Equation D = Density at 15°C, g/ml determined by Test Methods D 1298 or D 4052 DN = D – 0.85 B = $[e^{(-3.5)(DN)}] - 1$ T_{10} = 10 percent recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure T_{10N} = $T_{10} - 215$ T_{50} = 50 percent recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure T_{50N} = $T_{50} - 260$ T_{90} = 90 percent recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure T_{90N} = $T_{90} - 310$

Property	**Standard Test Method**	**Description**
Calculated Cetane Index	ASTM D 4737 – *Calculated Cetane Index by Four Variable Equations*	Use Procedure B for Grade No. 2–D S500. **Procedure B** CCI = -386.26 (D) + 0.1740 (T_{10}) + 0.1215 (T_{50}) + 0.01850 (T_{90}) + 297.42 Where: CCI = Calculated Cetane Index D = Density at 15°C, g/ml determined by Test Methods D 1298 or D 4052 T_{10} = 10 percent recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure T_{50} = 50 percent recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure T_{90} = 90 percent recovery temperature, °C, determined by test method D 86 and corrected to standard barometric pressure At the time of publication, Procedure B is commonly used to determine the Calculated Cetane Index of S15. Work is in progress at ASTM International to determine if a third procedure is required for ultra-low sulfur diesel fuels.
	ASTM D 976-80 – *Calculated Cetane Index of Distillate Fuels*	While this method is listed in Table 1 of ASTM D 975, its use is not recommended for low sulfur diesel fuel. ASTM D 4737 should be used for ultra-low sulfur diesel fuels in the U.S. ASTM D 976 is retained for use by the U.S. Navy and others outside the U.S. where they use high-sulfur distillates which can have higher aromatic levels and higher end points and where the Calculated Cetane Index determined by ASTM D 976 correlates better with the cetane number determined by ASTM D 613.

Property	Standard Test Method	Description
Derived Cetane Number	ASTM D 6890 – *Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber*	A small specimen of diesel fuel oil is injected into a heated, temperature-controlled constant volume chamber, which has previously been charged with compressed air. Each injection produces a single-shot, compression ignition combustion cycle. Ignition Delay (ID) is measured using sensors that detect the start of fuel injection and the start of significant combustion for each cycle. A complete sequence comprises 15 preliminary cycles and 32 further cycles. The ID measurements for the last 32 cycles are averaged to produce the ID result. An equation converts the ID result to a DCN.
	ASTM D 7170 – *Derived Cetane Number (DCN) of Diesel Fuel Oils – Fixed Range Injection Period, Constant Volume Combustion Chamber Method*	A small specimen of diesel fuel oil is injected into a heated, temperature-controlled constant volume chamber, which has previously been charged with compressed air. Each injection produces a single-shot, compression ignition combustion cycle. Ignition Delay (ID) is measured using sensors that detect the start of fuel injection and the start of significant combustion for each cycle. A complete sequence comprises two preliminary cycles and 25 further cycles. The ID measurements for the last 25 cycles are averaged to produce the ID result. An equation converts the ID result to a DCN.
Aromaticity Tests	ASTM D 1319 – *Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (IP 156)*	A small amount of sample is placed at the top of a special glass adsorption column packed with activated silica gel. The top layer of the silica gel in the column is treated with fluorescent dyes. Isopropyl alcohol is used to transport the sample and the fluorescent dyes down the column. Hydrocarbons are separated into bands of aromatics, olefins, and saturates according to their affinity for the silica gel. The fluorescent dyes are also selectively separated and make the boundaries of the aromatic, olefin, and saturate zones visible under ultraviolet light. The volume percentage of each hydrocarbon type is calculated from the length of each zone in the column.
	ASTM D 5186 – *Determination of Aromatic Content of Diesel Fuels by Supercritical Fluid Chromatography*	The sample is chromatographed on silica gel using supercritical carbon dioxide as the mobile phase to separate the aromatics from the rest of the sample and to separate the aromatics into monoaromatics and polycyclic aromatics.

Property	**Standard Test Method**	**Description**
Cloud Point	ASTM D 2500 – *Cloud Point of Petroleum Products (IP 219)*	A clean clear sample is cooled at a specified rate and examined periodically. The temperature at which a haze is first observed is the cloud point.
Pour Point	ASTM D 97 – *Pour Point of Petroleum Products (IP 15)*	A clean sample is first warmed and then cooled at a specified rate and observed at intervals of 3°C (5°F). The lowest temperature at which sample movement is observed when the sample container is tilted is the pour point.
Low-Temperature Operability	ASTM D 4539 – *Filterability of Diesel Fuels by Low-Temperature Flow Test (LTFT)*	A sample is cooled at a rate of 1°C/hour (1.8°F/hour) and filtered through a 17-micron screen under 20 kPa vacuum. The minimum temperature at which 180 milliliters can be filtered in one minute is recorded.
	ASTM D 6371 – *Cold Filter Plugging Point (CFPP) of Diesel and Heating Fuels (IP 309)*	A sample is cooled at a rate of about 40°C/hour. The highest temperature at which 20 milliliters of the fuel fails to pass through a 45-micron wire mesh under 2 kPa vacuum in less than 60 seconds is the CFPP.
Carbon Residue	ASTM D 524 – *Ramsbottom Carbon Residue of Petroleum Products (IP 14)*	The sample is first distilled (ASTM D 86) until 90 percent of the sample has been recovered. The residue is weighed into a special glass bulb and heated in a furnace to 550°C (1,022°F). Most of the sample evaporates or decomposes under these conditions. The bulb is cooled and the residue is weighed.
Lubricity	ASTM D 6079 – *Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR) (ISO/FDIS 12156-1(2005)(E))*	A hardened steel ball oscillates across a hardened steel plate under a fixed load for 75 minutes. The point of contact between the ball and plate is immersed in the sample. The size of the resulting wear scar on the steel ball is a measure of the sample's lubricity.
	ASTM D 6078 – *Evaluating Lubricity of Diesel Fuels by the Scuffing Load Ball-on-Cylinder Lubricity Evaluator (SLBOCLE)*	This test is based on the BOCLE test, but determines the maximum load that can be applied without causing scuffing. A ball-on-cylinder apparatus immersed in the sample is run under a series of loads to closely bracket the highest non-scuffing load the sample can tolerate.

Property	**Standard Test Method**	**Description**
Oxidation Stability	ASTM D 2274 – *Oxidation Stability of Distillate Fuel Oil (Accelerated Method) (IP 388)*	After filtration to remove any particulate contamination, a 350-milliliter sample is transferred to a special glass container and held at 95°C (203°F) for 16 hours while oxygen is bubbled through the sample. At the end of the treatment period, the sample is allowed to cool to room temperature and filtered to collect any insoluble material that formed. The adherent insolubles are washed off the glass container with a trisolvent (a mixture of equal parts methanol, toluene, and acetone); the trisolvent is evaporated to obtain the amount of adherent insolubles.
Storage Stability	ASTM D 4625 – *Distillate Fuel Storage Stability at 43°C (110°F) (IP 378)*	After filtration to remove any particulate contamination, separate 400-milliliter portions of the fuel are transferred to glass containers and stored at 43°C (110°F) for periods of 0, 4, 8, 12, 18, and 24 weeks. At the end of its treatment period, each sample is allowed to cool to room temperature and filtered to collect any insoluble material that formed. The adherent insolubles are washed off the glass container with a trisolvent; the trisolvent is evaporated to obtain the amount of adherent insolubles.
	ASTM D 5304 – *Assessing Distillate Fuel Storage Stability by Oxygen Over-Pressure*	After filtration to remove any particulate contamination, a 100-milliliter sample is placed in a glass container, which is placed in a pressure vessel preheated to 90°C (194°F). The vessel is pressurized with oxygen to 100 psig and then heated in an oven at 90°C for 16 hours. At the end of the treatment period, the sample is allowed to cool to room temperature and filtered to collect any insoluble material that formed. The adherent insolubles are washed off the glass container with a trisolvent; the trisolvent is evaporated to obtain the amount of adherent insolubles.

Property	Standard Test Method	Description
Thermal Stability	ASTM D 6468 – *High Temperature Stability of Distillate Fuels*	After filtration to remove any particulate contamination, separate 50-milliliter samples are placed in open tubes and aged for either 90 minutes or 180 minutes at 150°C (302°F) with air exposure. At the end of the treatment period, the samples are allowed to cool to room temperature and filtered. The amount of insoluble material collected on the filter pad is estimated by measuring the light reflected off of the pad.
Red Dye	ASTM D 6258 – *Determination of Solvent Red 164 Dye Concentration in Diesel Fuels*	Because the natural color of diesel fuels varies from nearly colorless to amber, red dye concentration cannot be measured accurately by simple visible absorption spectroscopy. This method effectively eliminates interference from the background color of the fuel by using the second derivative of the absorption spectrum. The amplitude difference between the second derivative spectrum maximum at 538 nanometers (nm) and the minimum at 561 nm is used to determine red dye concentration.
	ASTM D 6756 – *Determination of the Red Dye Concentration and Estimation of the ASTM Color of Diesel Fuel and Heating Oil Using a Portable Visible Spectrophotometer*	This test method describes the determination of the red dye concentration of diesel fuel and heating oil and the estimation of the ASTM color of undyed and red-dyed diesel fuel and heating oil. The test method is appropriate for use with diesel fuel and heating oil of Grades 1 and 2 described in Specifications D 396, D 975, D 2880, and D 3699. Red dye concentrations are determined at levels equivalent to 0.1 to 20 mg/L of Solvent Red 26 in samples with ASTM colors ranging from 0.5 to 5. The ASTM color of the base fuel of red-dyed samples with concentration levels equivalent to 0.1 to 20 mg/L of Solvent Red 26 is estimated for the ASTM color range from 0.5 to 5. The ASTM color of undyed samples is estimated over the ASTM color range of 0.5 to 5. The test method provides a means to indicate conformance to contractual and legal requirements.

Property	Standard Test Method	Description
Conductivity	ASTM D 2624 – *Electrical Conductivity of Aviation and Distillate Fuels (IP 274)*	ASTM D 2624 covers the use of portable conductivity meters and in-line conductivity meters to determine the electrical conductivity of aviation and distillate fuels with and without a static dissipator additive. The test methods normally give a measurement of the conductivity when the fuel is uncharged, that is, electrically at rest (known as the rest conductivity). A voltage is applied across two electrodes in the fuel and the resulting current expressed as a conductivity value. With portable meters, the current measurement is made almost instantaneously upon application of the voltage to avoid errors due to ion depletion. Ion depletion or polarization is eliminated in dynamic monitoring systems by continuous replacement of the sample in the measuring cell. The procedure, with the correct selection of electrode size and current measurement apparatus, can be used to measure conductivities from 1 pS/m or greater. Please see the sidebar on page 47 for the definition of conductivity.
	ASTM D 4308 – *Electrical Conductivity of Liquid Hydrocarbons by Precision Meter*	This test method applies to the determination of the "rest" electrical conductivity of aviation fuels and other similar low-conductivity hydrocarbon liquids in the range from 0.1 to 2,000 pS/m and can be used in the laboratory or in the field. A sample of liquid hydrocarbon is introduced into a clean conductivity cell which is connected in series to a battery voltage source and a sensitive dc ammeter. The conductivity, automatically calculated from the observed peak current reading dc voltage and cell constant using Ohm's law, appears as a digital value in either the manual or automatic mode of meter operation.

Table 5.8 lists the tests used to determine the properties of 100 percent methyl esters, or B100. (Several requirements are common to both diesel fuel and biodiesel fuel: cetane number, flash point, water and sediment, viscosity, sulfur, copper strip corrosion, and cloud point. These methods are described in Table 5.7.)

Table 5.8
Biodiesel Fuel Test Methods

Property	Standard Test Method	Description
Alcohol Control	EN 14110 – *Determination of Methanol Content* ASTM D 93 – *Flash-Point by Pensky-Martens Closed Cup Tester (IP 34)*	Alcohol control is to limit the level of unreacted alcohol remaining in the finished fuel. This can be measured directly by the volume percent alcohol or indirectly through a high flash point value. The flash point specification, when used for alcohol control for biodiesel, is intended to be 100°C minimum, which has been correlated to 0.2 vol % alcohol. Typical values are over 160°C. Due to high variability with Test Method D 93 as the flash point approaches 100°C, the flash point specification has been set at 130°C minimum to ensure an actual value of 100°C minimum. Improvements and alternatives to Test Method D 93 are being investigated. Once complete, the specification of 100°C minimum may be reevaluated for alcohol control.
Sulfated Ash	ASTM D 874 – *Sulfated Ash from Lubricating Oils and Additives (IP 163)*	Ash-forming materials may be present in biodiesel in three forms: (1) abrasive solids, (2) soluble metallic soaps, and (3) unremoved catalysts. Abrasive solids and unremoved catalysts can contribute to injector, fuel pump, piston and ring wear, and also to engine deposits. Soluble metallic soaps have little effect on wear but may contribute to filter plugging and engine deposits. The sample is ignited and burned until only ash and carbon remain. After cooling, the residue is treated with sulfuric acid and heated at 775°C until oxidation of carbon is complete. The ash is then cooled, re-treated with sulfuric acid, and heated at 775°C to constant weight.
Carbon Residue	ASTM D 4530 – *Determination of Carbon Residue (Micro Method)*	Carbon residue gives a measure of the carbon depositing tendencies of a fuel oil. While not directly correlating with engine deposits, this property is considered an approximation. Although biodiesel is in the distillate boiling range, most biodiesels boil at approximately the same temperature, and it is difficult to leave a 10 percent residual upon distillation. Thus, a 100 percent sample is used to replace the 10 percent residual sample, with the calculation executed as if it were the 10 percent residual.

Property	Standard Test Method	Description
Free and Total Glycerin	ASTM D 6584 – *Determination of Free Glycerin and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography*	The total glycerin method is used to determine the level of glycerin in the fuel and includes the free glycerin and the glycerin portion of any unreacted or partially reacted oil or fat. Low levels of total glycerin ensure that high conversion of the oil or fat into its mono-alkyl esters has taken place. High levels of mono-, di-, and triglycerides can cause injector deposits and may adversely affect cold weather operation and filter plugging. Free and bonded glycerin content reflects the quality of biodiesel. A high content of free glycerin may cause problems during storage by settling to the bottom of storage tanks, or in the fuel system by clogging fuel systems and injector deposits. A high total glycerin content can lead to injector fouling and may also contribute to the formation of deposits at injection nozzles, pistons, and valves. The sample is analyzed by gas chromatography, after silylating with N-methyl-N-trimethylsilyltrifluoracetamide (MSTFA). Calibration is achieved by the use of two internal standards and four reference materials. Mono-, di-, and triglycerides are determined by comparing to monoolein, diolein, and triolein standards respectively. Average conversion factors are applied to the mono-, di-, and triglycerides to calculate the bonded glycerin content of the sample.
Phosphorus	ASTM D 4951 – *Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry*	Phosphorus can damage catalytic converters used in emissions control systems and its level must be kept low. This specification was added to ensure that all biodiesel, regardless of the source, has low phosphorus content. A sample portion is weighed and diluted by mass with mixed xylenes or an other solvent. An internal standard, which is required, is either weighed separately into the test solution or is previously combined with the dilution solvent. Calibration standards are prepared similarly. The solutions are introduced to the Inductively Coupled Plasma (ICP) instrument by free aspiration or an optional peristaltic pump. By comparing emission intensities of elements in the test specimen with emission intensities measured with the calibration standards and by applying the appropriate internal standard correction, the concentration of phosphorus in the sample is calculable.

Property	**Standard Test Method**	**Description**
Distillation	ASTM D 1160 – *Distillation of Petroleum Products at Reduced Pressure*	Biodiesel exhibits a narrow boiling range rather than a distillation curve. The fatty acids chains in the raw oils and fats from which biodiesel is produced are mainly comprised of straight chain hydrocarbons with 16 to 18 carbons that have similar boiling temperatures. The atmospheric boiling point of biodiesel generally ranges from 330 to 357°C, thus the specification value of 360°C maximum at 90 percent recovered. This specification was incorporated as an added precaution to ensure the fuel has not been adulterated with high boiling contaminants. The sample is distilled at an accurately controlled pressure between 0.13 and 6.7 kPa (1- and 50-mm Hg) under conditions that are designed to provide approximately one theoretical plate fractionation. Data are obtained from which the initial boiling point, the final boiling point, and a distillation curve relating volume percent distilled and atmospheric equivalent boiling point temperature can be prepared.
Metals	EN 14538 – *Determination of Ca, K, Mg, and Na Content by Optical Emission Spectral Analysis with Inductively Coupled Plasma (ICP OES)*	Calcium, potassium, magnesium, and sodium may be present in biodiesel as abrasive solids or soluble metallic soaps. Abrasive solids can contribute to injector, fuel pump, piston, and ring wear and also to engine deposits. Soluble metallic soaps have little effect on wear, but they may contribute to filter plugging and engine deposits. High levels of these metals may also collect in diesel particulate filters and are not typically removed during passive or active regeneration. They can create increased back pressure and reduce the service maintenance period.
Stability	EN 14112 – *Determination of Oxidation Stability (Accelerated Oxidation Test), 743 Rancimat*	Determines the oxidation stability of biodiesel fuel. The sample is exposed to a stream of heated air. The volatile oxidation products are transferred to a measuring vessel by the air stream where they are absorbed into distilled water. The conductivity of the water is continuously measured. The time (in hours) between the start of the test and when the conductivity begins to increase rapidly is the induction period. This test provides an indication of the oxidation stability of the sample.

6 • Diesel Engines

Diesel engines have long been the workhorse of industry. Favored for their high torque output, durability, exceptional fuel economy and ability to provide power under a wide range of conditions, diesels are the dominant engines used in applications such as trucking, construction, farming, and mining. They are also extensively used for stationary power generation and marine propulsion and in passenger vehicles in many regions of the world. Diesel engines are not used widely in light-duty vehicles in the United States primarily because they do not meet U.S. emissions standards. However, because of significant improvements in diesel engine performance, injection technology, and exhaust aftertreatment devices, particulate matter and nitrogen oxides emissions have been reduced such that diesels are poised to achieve future emissions standards.[1]

Diesel engines are similar to gasoline engines in many ways. Both are internal combustion engines and most versions of them use a four-stroke cycle. There are four fundamental differences:

- The conventional gasoline engine injects fuel into the air as it is drawn into a cylinder. The diesel engine draws air into a cylinder and injects fuel after the air has been compressed. For a discussion about the Direct Injection Spark Ignition engine, please see the companion publication *Motor Gasoline Technical Review*.

- The gasoline engine ignites the fuel-air mixture with a spark. The diesel engine relies on high temperature alone for ignition. Diesel engines are often referred to as compression-ignition engines because this high temperature is the result of compressing air above the piston as it travels upward.

- The power output of a gasoline engine is controlled by a throttle, which varies the amount of fuel-air mixture drawn into a cylinder. A diesel engine does not throttle the intake air. It controls the power output by varying the amount of fuel injected into the air, thereby, varying the fuel-air ratio. This is one of the primary reasons that diesel engines are more fuel efficient than spark-ignition gasoline engines.

- A conventional gasoline engine runs stoichiometrically – the fuel-air ratio is fixed so that there is just enough air to burn all the fuel. A diesel engine runs lean – there is always more air than is needed to burn the fuel.

The main advantage of a diesel engine is its high thermal efficiency.[2] Diesel engines can achieve thermal efficiencies in excess of 50 percent. The best conventional gasoline engines are approximately from 30 to 33 percent efficient, and then only at wide throttle openings. As a result, diesel engines have better fuel economy than gasoline engines.

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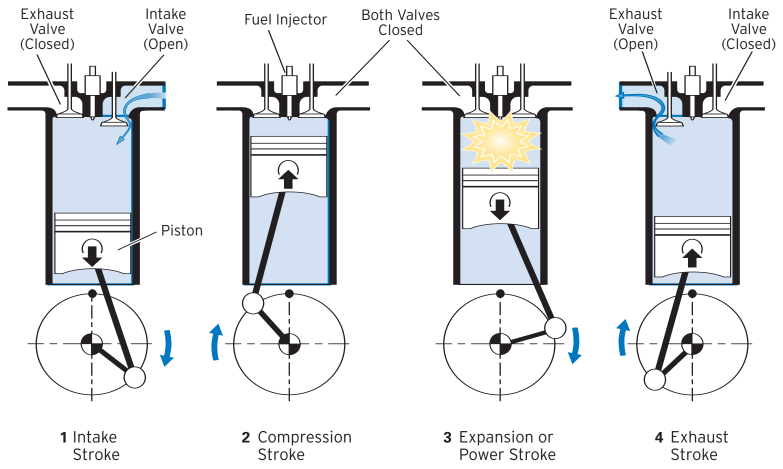
1 Green, David L., Duleep, K.G., and McManus, Walter: “Future Potential of Hybrid and Diesel Powertrains in the U.S. Light-Duty Vehicle Market, “ ORNL/TM-2004/181, Oak Ridge National Laboratory, U/S. Department of Energy, Knoxville, Tennessee, (August 2004).

2 Thermal efficiency is defined as the amount of work produced by the engine divided by the amount of chemical energy in the fuel that can be released through combustion. This chemical energy is often referred to as net heating value or heat of combustion of the fuel.

FOUR-STROKE CYCLE

By far the most common type of diesel engine used today has reciprocating pistons and uses a four-stroke operating cycle (see Figure 6.1). In the first stroke (intake stroke), the intake valve opens while the piston moves down from its highest position in the cylinder (closest to the cylinder head) to its lowest position. This draws air into the cylinder in the process. In the second stroke (compression stroke), the intake valve closes and the piston moves back up the cylinder. This compresses the air and, consequently, heats it to a high temperature, typically in excess of 540°C (1,000°F). Near the end of the compression stroke, fuel is injected into the cylinder. After a short delay, the fuel ignites spontaneously, a process called autoignition. The hot gases produced by combustion of the fuel further increase the pressure in the cylinder, forcing the piston down (expansion stroke or power stroke); the combustion energy is transformed into mechanical energy. The exhaust valve opens when the piston is again near its lowest position, so that as the piston once more moves to its highest position (exhaust stroke), most of the burned gases are forced out of the cylinder.

Figure 6.1
Four-Stroke Cycle



Fuel injection begins shortly before the end of the compression stroke.

ENGINE ABBREVIATIONS

The reciprocating piston engine has its own set of abbreviations:

- *The position in the cycle when the piston is at the top of its stroke is called top dead center (TDC).*
- *When the piston is at its lowest point, it is called bottom dead center (BDC).*
- *The angle of crankshaft rotation from TDC is expressed in crank angle degrees (CAD), with TDC defined as zero degrees. A complete four-stroke cycle involves a crankshaft rotation of 720 CAD, 180 CAD for each stroke. A two-stroke cycle involves a rotation of only 360 CAD.*
- *The point of fuel injection is expressed in terms of CAD before TDC (BTDC), e.g., 13° BTDC.*
- *Valve opening and closing times are also expressed in CAD before or after TDC (ATDC).*

Figure 6.2
Direct-Injection (DI) Process

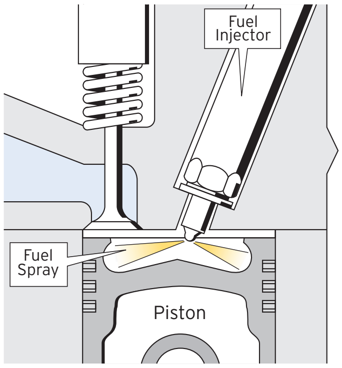
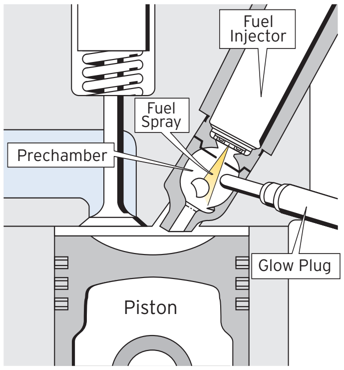


Figure 6.3
Indirect-Injection (IDI) Process



COMPRESSION RATIO

An important parameter of an engine is its compression ratio. This is defined as the ratio of the volume of the cylinder at the beginning of the compression stroke (when the piston is at BDC) to the volume of the cylinder at the end of the compression stroke (when the piston is at TDC). The higher the compression ratio, the higher the air temperature in the cylinder at the end of the compression stroke will be.

Higher compression ratios, to a point, lead to higher thermal efficiencies and better fuel economy. Diesel engines need high compression ratios to generate the high temperatures required for fuel autoignition. Conversely, gasoline engines use lower compression ratios in order to avoid fuel autoignition, which manifests itself as engine knock (often heard as a pinging sound).

COMBUSTION CHAMBERS

Direct-Injection and Indirect-Injection

The two basic types of four-stroke diesel engines, direct-injection (DI) and indirect-injection (IDI), are illustrated in Figures 6.2 and 6.3. In a DI engine, fuel is injected directly into the cylinder above the piston.

In an IDI engine, also known as a prechamber engine, fuel is injected into a small prechamber connected to the cylinder through a narrow passage that enters the prechamber tangentially. During the compression process, air is forced through this passage, generating a vigorous swirling motion in the prechamber. Fuel is then injected into the prechamber and ignition occurs there. The combination of rapidly swirling air in the prechamber and the jet-like expansion of combustion gases from the prechamber into the cylinder enhance the mixing and combustion of fuel and air.

The more rapid mixing of fuel and air achieved in IDI engines comes at a price, however. The high-velocity flow of air through the narrow passage connecting the main cylinder to the prechamber, and the vigorous swirling motion in the prechamber itself, cause the air to lose significantly more heat during compression than it does in a DI engine. These actions, coupled with a pressure drop from the main chamber to the prechamber, result in an air temperature in the prechamber after compression that is lower than that in a similar DI engine.

Because rapid fuel autoignition requires a certain air temperature, an IDI engine needs a higher compression ratio to achieve the desired air temperature in the prechamber. IDI engines operate at compression ratios of about 20:1 to 24:1; while DI engines operate at ratios of about 15:1 to 18:1. The heat losses that necessitate these higher compression ratios have a significant downside: they decrease the efficiency of the engine. IDI engines typically achieve fuel efficiencies that are from 10 to 20 percent lower, on a relative basis, than comparable DI engines.

Even with the higher compression ratio, IDI engines may still be hard to start. Most IDI engines use glow plugs to heat the air in the prechamber to make starting easier. Glow plugs, which are small resistive heaters, are usually only powered for the first few minutes of engine operation.

With the negative attributes of harder starting and lower efficiency, one may wonder why IDI diesel engines are used at all. The answer is engine speed. As an engine gets smaller, generally, it must operate at higher speeds to generate the desired power. As engine speed increases, there is less time per engine cycle to inject, vaporize, mix, and combust the fuel. As a result, the higher mixing rates, afforded by IDI designs, become necessary to achieve good combustion at higher engine speeds.

IDI diesels most commonly were used in smaller automotive and light-duty truck applications. New engine design and advanced technology has eliminated the need for IDI engines in these higher-speed small-engine applications. Most new engines today are DI engines.

TURBOCHARGING, SUPERCHARGING, AND CHARGE COOLING

It is common practice to employ some form of forced air induction to increase maximum power because the power output of diesel engines (or for that matter, gasoline engines) is limited by the amount of air they take in. In turbocharging or supercharging, a compressor is used to raise the pressure and, therefore, the density of the air entering the engine. Increasing the total mass of air inducted per cycle allows more fuel to be injected and burned without increasing the fuel-air ratio to the point that particulate emissions become excessive (smoke limit).

Even at equal power, a forced-air diesel engine has an advantage over a naturally aspirated engine. The increased air mass decreases the fuel-air ratio and thereby improves the engine's thermal efficiency (fuel economy). In addition, the decrease in the fuel-air ratio at part power can also improve emissions performance, depending on other factors.

Turbocharging

Turbocharging uses a small exhaust-gas-driven turbine to drive a similarly small compressor located on the same shaft to pressurize the intake air. Thus, the energy for compressing the intake air is scavenged from the exhaust, which makes this method more efficient than supercharging. Turbochargers are more commonly used than superchargers, but have two disadvantages:

- There can be a lag (turbo lag) between the time that the driver demands more power and the time when the intake air pressure reaches its maximum.
- Turbochargers must operate at high temperatures and high rotational speeds. Appropriate design, combined with the typical operating conditions of most diesel engines, has almost eliminated these mechanical concerns.

Supercharging

Supercharging uses a mechanically driven pump to pressurize the intake air. Several types of pumps are commonly employed; almost all are positive-displacement pumps and all are driven by the engine crankshaft, either directly or by gears or belts. Like turbocharging, supercharging can improve thermal efficiency and boost power output. However, because supercharging uses work from the crankshaft to power the compressor, the degree of compression depends upon engine speed, instead of engine load (power output), eliminating the power lag that can occur with a turbocharger.

Both turbocharging and supercharging compress the intake air and increase its temperature and density. This temperature increase is counterproductive, because air density is inversely proportional to temperature, i.e., the hotter the air, the less dense it becomes. An additional increase in density can be achieved by cooling the hot compressed air before it enters the engine. Charge cooling, also referred to as intercooling or aftercooling, passes the hot compressed air coming from the compressor through a heat exchanger (similar in design to a radiator) to lower its temperature. Charge cooling can provide significant gains in power output. It also can decrease NO_x emissions (see page 81).

FUEL INJECTION SYSTEMS

As described above, liquid fuel is injected into the hot compressed air late in the compression stroke shortly before the piston reaches TDC. This fuel must vaporize and mix with the air in order to burn. Complete mixing is essential for complete combustion and any fuel that does not burn completely will contribute to hydrocarbon and particulate emissions. The quantity of fuel injected into the cylinder must be less than stoichiometric because complete mixing of all fuel and air in the cylinder can never be totally achieved – it is limited by the amount of air present and the effectiveness of the mixing processes. Diesel engines are typically controlled to a maximum fuel-air ratio to limit the amount of particulate emissions (smoke limit) produced by the engine. However, this control also limits the power output of the engine.

Fuel is injected under high pressure up to 30,000 psi (200 MPa or 2,000 bar) into the combustion chamber through a fine nozzle. The injection system is designed to produce a fine spray of small fuel droplets that will evaporate quickly in order to facilitate rapid mixing of fuel vapor and air. Other engine design features that facilitate mixing include optimizing the position and angle of the nozzle in the cylinder head and sculpting the piston tops and intake ports to generate a swirling motion of the gases in the cylinder.

Modern fuel injection systems are not only responsible for injection timing, atomization, and injection quality, they also provide several additional functions – rate shaping (or scheduling the injection of fuel), multiple injections, pilot injection, and post injection.

Rate shaping is important to the performance, emissions and noise characteristics of the combustion process. Multiple injections in a single combustion cycle allows for changing load conditions and engine speed. Pilot injection decreases noise and cold-start smoke formation. Emissions aftertreatment devices, such as diesel particulate filters and NO_x adsorber/catalysts, require regeneration facilitated by increased exhaust temperatures and/or by "rich" exhaust gas of increased hydrocarbon (HC) content. The post injection can achieve both purposes.[3]

These features are fulfilled by the common rail injection system. The common rail injection system consists of a high-pressure fuel pump, a rail for fuel storage and distribution, electrohydraulic injectors, and the electronic control unit (ECU). Injection pressure is generated independent of engine speed and injected fuel quantity, and it is stored, ready for each injection process, in the rail. The start of injection and the injected fuel quantity are calculated in the ECU and implemented by the injection unit at each cylinder through a triggered solenoid valve.[4]

ELECTRONIC ENGINE CONTROLS

Better control of the combustion process is critical if modern diesel engines are to meet the demands of high power output, fuel economy, durability, and low levels of emissions. In a diesel engine, this means controlling both the amount of fuel that is injected during each engine cycle and the rate at which it is injected.

Historically, diesel engines employed mechanical systems to inject fuel into the combustion chamber. While mechanical injectors effectively achieve the required high injection pressures at reasonable cost, they operate in a fixed, predetermined way. Thus, they are not easily adaptable to modern methods of control.

Currently, electronic engine controls and electronic injectors are being used to control fuel injection more carefully. These systems employ a variety of sensors to monitor how the engine is operating by measuring such variables as: engine speed, load demand ("throttle" position), engine coolant and exhaust temperatures, and air temperature and pressure (or mass flow rate). A microprocessor interprets the sensor outputs and generates signals to operate the electronic fuel injectors. In this way, the total quantity of fuel and the rate at which it is injected (the injection profile) are optimized for the instantaneous engine conditions.

Electronic engine controls are more expensive than traditional mechanical injection systems. Fortunately, the rapid evolution of microprocessors has made it possible to produce high-powered systems at an acceptable cost. In many cases, the initial cost of electronic engine control will be more than offset by the savings from increased fuel efficiency.

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3 "Diesel Fuel Injection," DieselNet Technology Guide, Ecopoint, Inc., http://www.dieselnet.com

4 "Diesel-Engine Management," second edition, Robert Bosch GmbH, Stuttgart (1999).

MARINE DIESEL ENGINES

Large marine diesels operate on the same principles as automotive DI diesels, but on a much larger scale. The pistons can be three feet (one meter) in diameter with a six-foot (two-meter) stroke. Because of the high mechanical stress involved with moving the large pistons, they operate at lower speeds of 70 to 100 rpm. These slow speeds mean that, these engines do not usually employ methods, such as swirl, to enhance mixing of fuel and air as they are unnecessary. These engines typically have compression ratios of 10:1 to 12:1 and can have thermal efficiencies of up to 55 percent.

TWO-STROKE CYCLE

Two-stroke cycle diesel engines are very similar to four-stroke cycle engines, except that they do not have separate intake and exhaust strokes. Instead, exhaust occurs at the end of the expansion, or power, stroke and continues into the early part of the compression stroke. Intake occurs during the end of the expansion stroke and the early part of the compression stroke. To assist the intake process, the intake air is almost always boosted above atmospheric pressure using supercharging or turbocharging. Air flow into the cylinder and exhaust gas flow out of the cylinder are controlled by conventional poppet valves in the cylinder head, ports in the cylinder wall, or a combination of both.

The advantage of the two-stroke cycle is that it generates more power for a given engine size because power is generated on every other stroke, rather than every fourth stroke. The disadvantages are that emissions are higher with a two-stroke cycle than with a four-stroke cycle, and fuel efficiency can be marginally poorer. At one time, two-stroke cycle diesel engines were very popular because of their high power density. Their popularity has diminished for the many uses where low emissions are important. However, they are still common in uses such as large marine engines, where poor emissions performance is only beginning to become an issue.

DIESEL ENGINES AND EMISSIONS

Exhaust emissions are the Achilles' heel of diesel engines. Diesel exhaust tends to be high in NO_x and particulates, both visible (smoke) and invisible. Both NO_x and particulates are significant environmental pollutants. Unlike the exhaust of gasoline engines, diesel exhaust contains much less unburned or partially burned hydrocarbons and carbon monoxide. Because of the importance of diesel emissions, it is worthwhile taking a closer look at the combustion process to see how they are formed. This discussion is necessarily superficial because the physical and chemical processes taking place in a cylinder during combustion are very complex – and not completely understood.

As fuel is injected into a cylinder under high pressure, it atomizes into small droplets and begins to evaporate as it moves away from the nozzle. The fuel-air ratio at any point in the cylinder may range from zero, at a point with no fuel, to infinity inside a fuel droplet that has not yet vaporized. In general, the fuel-air ratio is high near the nozzle tip and low away from it, but because of the complexity of the mixing process, the fuel-air ratio does not change uniformly within the cylinder. Combustion can only occur within a certain range of the fuel-air ratio. If the ratio is too low, there is not enough fuel to support combustion and if the ratio is too high, there is not enough air.

As the fuel vaporizes into the hot air, it starts to oxidize. When more fuel vaporizes and mixes with air, the number and rate of oxidation reactions increase until the end of the ignition delay period. At that time, ignition occurs at many locations independently and combustion propagates very rapidly in regions having fuel-air ratios in the combustible range. This initial combustion after ignition is called the pre-mixed combustion phase. It consumes approximately 5 to 10 percent of the fuel used by the engine at typical full-load operation.

At the end of the pre-mixed combustion phase most of the fuel has yet to be injected or is still in a region that is too rich to burn. However, injection continues and fuel continues to vaporize and mix with air aided by the heat release and turbulence generated by the initial combustion. This quickly generates more gas with the required fuel-air ratio and combustion continues. The process, called the diffusion controlled or mixing controlled phase of combustion, ideally consumes all of the remaining fuel.

This background information provides a better understanding of how pollutants are formed during combustion in a diesel engine. NO_x, hydrocarbons, CO, and particulates are all formed under different conditions and by different mechanisms.

Nitrogen Oxides

NO and NO_2 tend to form in the stoichiometric and slightly lean regions where there is excess oxygen and the temperature is high. (See *Chapter 3 – Diesel Fuel and Air Quality.*) Outside of these regions, either there is insufficient oxygen to form NO_x or temperatures are too low for the reactions to occur quickly enough.

Hydrocarbons

HC emissions can be either unburned or partially burned fuel molecules and can come from several sources. At ignition, some of the vaporized fuel will already be in a region that is too lean for it to burn and, unless it burns later in the cycle, this fuel will be emitted. The cylinder walls and “crevice” regions around the top of the piston edge and above the rings are much cooler than the combustion gases and tend to quench flames as they encroach. Thus, fuel at the cylinder wall can contribute to HC emissions. Fuel that does not vaporize during a cold start makes up the white smoke seen under this condition. A small amount of fuel can also dissolve in the thin film of lubricating oil on the cylinder wall, be desorbed in the expansion stroke, and then emitted. However, since diesel engines operate at an overall lean fuel-air ratio, they tend to emit low levels of hydrocarbons.

Carbon Monoxide

CO is a result of incomplete combustion. It mostly forms in regions of the cylinder that are too fuel-rich to support complete combustion; although, it may also originate at the lean limit of combustible fuel-air mixtures. If temperatures are high enough, the CO can further react with oxygen to form CO_2. Because diesel engines have excess oxygen, CO emissions are generally low.

Particulates

Some of the fuel droplets may never vaporize and/or mix with air, and thus, never burn. However, the fuel doesn't remain unchanged because the high temperatures in the cylinder cause it to decompose. Later, this fuel may be partly or completely burned in the turbulent flame. If it is not completely burned, it will be emitted as droplets of heavy liquid or particles of carbonaceous material. The conversion of fuel to particulates is most likely to occur when the last bit of fuel is injected in a cycle, or when the engine is being operated at high load and high speed. At higher engine speeds and loads, the total amount of fuel injected increases and the time available for combustion decreases. In addition, some of the lubricating oil on the cylinder wall is partially burned and contributes to particulate emissions. Finally, a poorly operating or mistimed fuel injection system can substantially increase emissions of particulates.

EMISSION REDUCTION TECHNOLOGIES

A modern diesel engine that has been well maintained emits much less smoke and other pollutants than older engines. This section looks at some of the approaches taken to reduce diesel engine emissions.

The design of the combustion system is the most important factor in determining emissions. Fuel plays a secondary, but still significant, role. Many advances in combustion system design in recent years have led to a reduction in the formation of emissions including:

- **Higher Injection Pressures** This leads to better atomization and smaller fuel droplets, which vaporize more readily than larger droplets.

- **Careful Injection Targeting** The position and angle of the injector in the cylinder head and the design of the nozzle are optimized to minimize emissions.

- **Charge Shaping** The rate of fuel (charge) injection can be controlled deliberately (shaped) during injection to achieve desired effects. For example, a small amount of fuel can be injected early and allowed to ignite before the rest of the charge is injected. Early injection acts like a pilot light for the main injection. Other strategies are also used and they are optimized for each engine design.

- **More Air Motion** The cylinder head, air intake valve, and piston head are designed to provide optimal air motion for better fuel-air mixing.
- **Charge Cooling (Forced Air Induction Engines)** As described earlier, most diesel engines employ supercharging or turbocharging in order to increase the maximum power. In these designs, an engine-driven or an exhaust-driven pump is used to force more air into the cylinders by compressing it. Compressing or pressurizing the intake air also heats it. Because NO_x formation is very sensitive to temperature, this also tends to increase NO_x emissions. However, this effect can be mitigated by cooling the intake air by passing it through a heat exchanger after it has been compressed by the supercharger or turbocharger, before it enters the engine cylinder.
- **Lower Oil Consumption** Diesel engines partially burn some of the crankcase lubricating oil that seeps past the piston rings into the combustion chamber. New designs minimize oil seepage.
- **Exhaust Gas Recirculation (EGR)** As mentioned above, the formation of NO_x is strongly affected by the temperature in the combustion chamber. This temperature can be reduced somewhat by diluting the reaction mixture with an inert gas. The maximum temperature of the combustion gas is reduced because some of the heat generated by combustion must be used to heat this inert gas. Because engine exhaust is essentially inert, it can be used for this purpose. EGR circulates a portion of the exhaust gas back to the air intake manifold. The reduction in NO_x is accompanied by a small loss of power.

In addition to these changes to minimize the production of pollutants, there are also exhaust aftertreatment systems designed to remove pollutants from the exhaust gas.

Exhaust Aftertreatment Systems

Particulate traps, or filters, filter the exhaust gas before it is released to the atmosphere. Diesel particulate filters remove from 70 to 90 percent of the particulate matter from the exhaust. The particulates build up in the traps over time and must be removed by burning because they are mainly carbon. Some designs use electrical resistance heaters to raise the temperature in the trap high enough to burn off the particulates. Others have built a burner into the trap. More exotic designs use plasma and microwave energy. In one system, a catalyst is used to lower the regeneration temperature. Currently, the most common regeneration scheme employs “post injection,” in which a small amount of fuel is injected into the cylinder late in the expansion stroke. This fuel then burns in the exhaust system, raising the trap temperature to the point where the accumulated particulate matter is readily burned away. As might be expected, however, this scheme does carry a fuel economy penalty of a few percent. Research is underway to achieve more effective and more easily regenerated traps.

Catalytic converters can be used to remove HC and CO from diesel exhaust. Oxidation catalysts, similar to those used in gasoline cars, convert unburned hydrocarbons and carbon monoxide to carbon dioxide and water. These converters are not as effective as the ones in gasoline vehicles. The particulates in the exhaust gas build up on the catalyst and physically block the exhaust gases from the catalyst's surface. The cooler temperature of diesel engine exhaust, compared to gasoline engine exhaust, also reduces catalyst efficiency. Fortunately, hydrocarbon and carbon monoxide emissions from diesel engines are inherently low, so that aftertreatment to remove these pollutants is rarely needed.

Probably the biggest emissions challenge for designers of diesel engines is reducing NO_x emissions. The high combustion temperatures in a diesel engine favor NO_x formation. EGR can be used to lower NO_x formation, but removing NO_x from exhaust gases involves reducing it to diatomic nitrogen (N_2). This is a challenge because the excess oxygen in diesel exhaust makes it an oxidizing environment. Oxidation and reduction are opposing chemical tendencies; conditions that favor oxidation are generally unfavorable to reduction. The development of a "lean NO_x" catalyst, one that will reduce NO_x in a lean or excess-oxygen environment, is an area of active research.

Another approach to converting NO_x to nitrogen is selective catalytic reduction (SCR). It is a cost-effective method for reducing emissions and has been used for years in stationary applications. In an SCR system, urea dissolved in water is sprayed into the exhaust system ahead of an SCR catalyst. The urea, held in a separate tank, produces ammonia, which reacts with NO_x over the SCR catalyst to form nitrogen, carbon dioxide, and water. It is capable of achieving a 90 percent reduction of NO_x emissions while reducing HC and CO emissions by 50 percent to 90 percent and PM emissions by 30 to 50 percent. SCR is currently fitted to most new heavy-duty diesel engines in Europe and to some engines in Japan and the U.S. Systems are also being developed for light-duty vehicles, with proposed introduction into the U.S. market in about 2010.

With the increased stringency of diesel emissions limits, no single technology is usually sufficient to achieve all emissions requirements. Diesel-powered vehicles are now regularly designed with emissions control systems that combine multiple elements. For example, a system may incorporate advanced combustion control with common-rail injection, a diesel particulate filter, followed by an SCR or NO_x adsorber, and, finally, an oxidation catalyst. These systems add significant cost and carry a fuel economy penalty, but can provide impressive reductions in tailpipe emissions.

7 • Diesel Fuel Additives

The first part of this chapter describes the additives that are used in diesel fuel – what they are and why and how they work. The second part of the chapter describes their use in practice.

TYPES OF ADDITIVES

Diesel fuel additives are used for a wide variety of purposes. Four applicable areas are:

- Engine and fuel delivery system performance
- Fuel handling
- Fuel stability
- Contaminant control

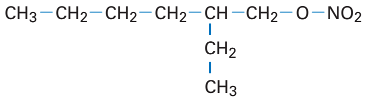
Engine and Fuel Delivery System Performance Additives

This class of additives can improve engine or injection system performance. The effects of different members of the class are seen in different time frames. Any benefit provided by a cetane number improver is immediate, whereas that provided by detergent additives or lubricity additives is typically seen over the long term, often measured in thousands or tens of thousands of miles.

Cetane Number Improvers (Diesel Ignition Improvers)

Cetane number improvers raise the cetane number of the fuel. Within a certain range, a higher number can reduce combustion noise and smoke and enhance ease of starting the engine in cold climates. The magnitude of the benefit varies among engine designs and operating modes, ranging from no effect to readily perceptible improvement.

Cetane Number Improver



$CH_3-CH_2-CH_2-CH_2-\underset{\substack{|\\ CH_2\\ |\\ CH_3}}{CH}-CH_2-O-NO_2$

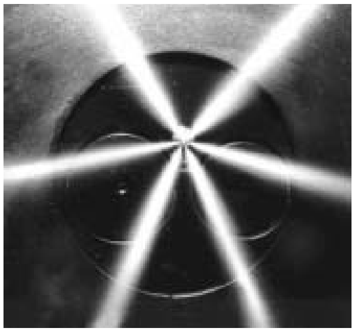
2-Ethylhexyl nitrate

2-Ethylhexyl nitrate (EHN) is the most widely used cetane number improver. It is also called octyl nitrate. EHN is thermally unstable and decomposes rapidly at the high temperatures in the combustion chamber. The products of decomposition help initiate fuel combustion and thus shorten the ignition delay period from that of the fuel without the additive.

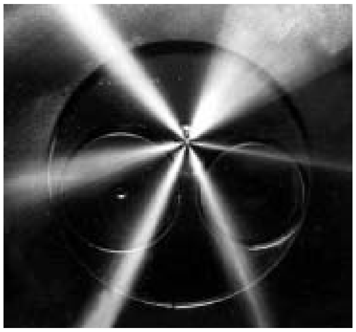
The increase in cetane number from a given concentration of EHN varies from one fuel to another. It is greater for a fuel whose natural cetane number is already relatively high. The incremental increase gets smaller as more EHN is added, so there is little benefit to exceeding a certain concentration. EHN typically is used in the concentration range from 0.05 to 0.4 percent mass and may yield a three to eight cetane number benefit. A disadvantage of EHN is that it decreases the thermal stability of some diesel fuels. This can be compensated for by the use of thermal stability additives.

Figure 7.1

Fuel Spray Pattern



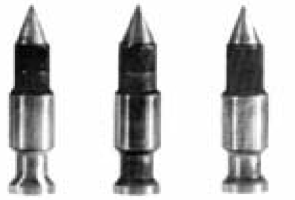
Clean injector – regular spray pattern



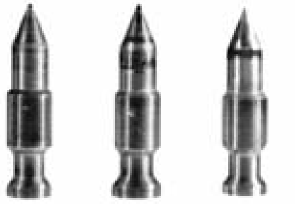
Deposited injector – irregular spray pattern

Figure 7.2

Typical Deposit Levels on a Fuel Injector Plunger Susceptible to Deposit Formation



Untreated fuel



Fuel with deposit control additive

Di-tertiary butyl peroxide (DTBP) is another additive which is used commercially as a diesel cetane improver; it is a less effective cetane number improver than EHN. However, DTBP does not degrade thermal stability of most diesel fuels, and it does not contain nitrogen (which may be important for meeting some reformulated diesel fuel regulatory requirements).

Other alkyl nitrates, as well as ether nitrates, peroxides, and some nitroso compounds, have also been found to be effective cetane number improvers, but most are not used commercially. The effects of these other cetane number improvers on other fuel properties, such as thermal stability, is not fully known.

Injector Cleanliness Additives

Fuel and/or crankcase lubricant can form deposits in the nozzle area of injectors – the area exposed to high cylinder temperatures. The extent of deposit formation varies with engine design, fuel composition, lubricant composition, and operating conditions. Excessive deposits may upset the injector spray pattern (see Figure 7.1) which, in turn, may hinder the fuel-air mixing process. In some engines, this may result in decreased fuel economy and increased emissions.

Ashless polymeric detergent additives can clean up fuel injector deposits and/or keep injectors clean (see Figure 7.2). These additives are composed of a polar group that bonds to deposits and deposit precursors, and a non-polar group that dissolves in the fuel. Thus, the additive can redissolve deposits that already have formed and reduce the opportunity for deposit precursors to form deposits. Detergent additives typically are used in the concentration range of 50 to 300 ppm.

Lubricity Additives

Lubricity additives are used to compensate for the lower lubricity of severely hydrotreated diesel fuels. (See *Chapter 2 – Diesel Fuel and Driving Performance.)* They contain a polar group that is attracted to metal surfaces that causes the additive to form a thin surface film. The film acts as a boundary lubricant when two metal surfaces come in contact.

Three additive chemistries, mono acids, amides, and esters, are commonly used. Mono acids are more effective, therefore lower concentrations are used (10 to 50 ppm). Because esters and amides are less polar, they require a higher concentration range from 50 to 250 ppm. Most ultra-low sulfur diesel fuels need a lubricity additive to meet the ASTM D 975 and EN 590 lubricity specifications.

Smoke Suppressants

Some organometallic compounds act as combustion catalysts. Adding these compounds to fuel can reduce the black smoke emissions that result from incomplete combustion. Such benefits are most significant when used with older technology engines which are significant smoke producers.

There is significant concern regarding potential toxicological effects and engine component compatibility with metallic additives in general. During the 1960s, before the Clean Air Act and the formation of the U.S. EPA, certain barium organometallics were occasionally used in the U.S. as smoke suppressants. The EPA subsequently banned them because of the potential health hazard of barium in the exhaust.

Smoke suppressants based on other metals, e.g., iron, cerium, or platinum, continue to see limited use in some parts of the world where the emissions reduction benefits may outweigh the potential health hazards of exposure to these materials. Use of metallic fuel additives is not currently allowed in the U.S., Japan, and certain other countries.

Fuel Handling Additives

Antifoam Additives

Some diesel fuels tend to foam as they are pumped into vehicle tanks. The foaming can interfere with filling the tank completely or result in a spill. Most antifoam additives are organosilicone compounds and are typically used at concentrations of 10 ppm or lower.

De-Icing Additives

Free water in diesel fuel freezes at low temperatures. The resulting ice crystals can plug fuel lines or filters, blocking fuel flow. Low molecular weight alcohols or glycols can be added to diesel fuel to prevent ice formation. The alcohols/glycols preferentially dissolve in the free water giving the resulting mixture a lower freezing point than that of pure water.

Low-Temperature Operability Additives

There are additives that can lower a diesel fuel's pour point (gel point) or cloud point or improve its cold flow properties (see pages 7 and 56). Most of these additives are polymers that interact with the wax crystals that form in diesel fuel when it is cooled below the cloud point (see sidebar on page 8). The polymers mitigate the effect of wax crystals on fuel flow by modifying their size, shape, and/or degree of agglomeration. The polymer-wax interactions are fairly specific; a particular additive generally will not perform equally well in all fuels.

The additives can be broken down into three idealized groups:

- Specialized additives for narrow boiling range fuels
- General purpose additives
- Specialized additives for high final boiling point fuels

To be effective, the additives must be blended into the fuel before any wax has formed, i.e., when the fuel is above its cloud point. The best additive and treat rate[1] for a particular fuel cannot be predicted; it must be determined experimentally. Some cloud point depressant additives also provide lubricity improvements.

The benefits that can be expected from different types of low temperature operability additives are listed in Table 7.1.

Table 7.1

Low-Temperature Operability Additive Benefits

Additive Type	Typical Treatment Rate, ppm	Typical Benefit*	
		°C	°F
Cloud Point	200 to 2,000	3 to 4	5 to 7
LTFT	50 to 2,000	8 to 12	15 to 25
CFPP	100 to 2,000	15 to 20	25 to 35
Pour Point	100 to 300	30 to 40	50 to 70

* Reduction from value for unadditized fuel.

Conductivity Additives

When fuel is pumped from one tank to another (in a refinery, terminal, or fueling station), especially when pumped through a filter, a small amount of static electric charge is generated. Normally, this charge is quickly dissipated and does not pose a problem. However, if the conductivity of the fuel is low, the fuel may act as an insulator allowing a significant amount of charge to accumulate. Static discharge may then occur posing a potential risk of fire hazard. Typically, the lower-sulfur diesel fuels have lower conductivity.

In order to prevent static charge accumulation, anti-static additives can be used to improve the electrical conductivity of fuel. Anti-static additives are available in both metallic and non-metallic chemistries (metallic additives are banned by the U.S. EPA for use in the United States), and are typically used at concentrations of 10 ppm or less.

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[1] Treat rate or treatment rate is the concentration of the additive in the fuel.

Drag Reducing Additives
Pipeline companies sometimes use drag reducing additives to increase the volume of product they can deliver. These high molecular weight polymers change the turbulent flow characteristics of fluids flowing in a pipeline, which can increase the maximum flow rate from 20 to 40 percent. Drag reducing additives are typically used in concentrations below 15 ppm. When the additized product passes through a pump, the additive is broken down (sheared) into smaller molecules that have minimal effect on product performance in engines at normal operating temperatures.

Fuel Stability Additives

Fuel instability results in the formation of gums that can lead to injector deposits or particulates that can plug fuel filters or the fuel injection system. The need for a stability additive varies widely from one fuel to another. It depends on how the fuel was made – the crude oil source and the refinery processing and blending. Stability additives typically work by blocking one step in a multi-step reaction pathway (see page 37). Because of the complex chemistry involved, an additive that is effective in one fuel may not work as well in another.

If a fuel needs to be stabilized, it should be tested to select an effective additive and treat rate. Best results are obtained when the additive is added immediately after the fuel is manufactured. S15 diesel fuels will probably be more thermally stable, but may be prone to peroxide formation during storage.

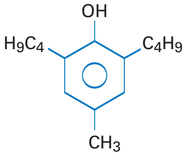
Antioxidants
One mode of fuel instability is oxidation. Oxidation takes place when oxygen, in the small amount of dissolved air, attacks reactive compounds in the fuel. This initial attack sets off complex chain reactions.

Antioxidants work by interrupting the chain reactions. Hindered phenols and certain amines, such as phenylenediamine, are the most commonly used antioxidants. They typically are used in the concentration range from 10 to 80 ppm.

Stabilizers
Acid-base reactions are another mode of fuel instability. The stabilizers used to prevent these reactions typically are strongly basic amines and are used in the concentration range from 50 to 150 ppm. They react with weakly acidic compounds to form products that remain dissolved in the fuel and do not react further.

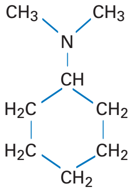
Metal Deactivators
When trace amounts of certain metals, especially copper and iron, are dissolved in diesel fuel, they catalyze (accelerate) the reactions involved in fuel instability. Metal deactivators tie up (chelate) these metals and neutralize their catalytic effect. They are typically used in the concentration range from 1 to 15 ppm.

Antioxidant



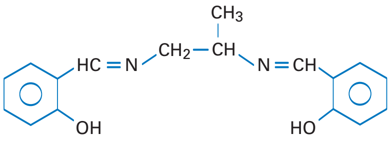
2,6-Di-t-butyl-4-methyl phenol

Stabilizer



N, N-Dimethylcyclohexyl amine

Metal Deactivator



N, N-Disalicylidene-1,2-propanediamine (DMD)

Dispersants

Multi-component fuel stabilizer packages may contain a dispersant. The dispersant doesn’t prevent the fuel instability reactions; however, it does disperse the particulates that form preventing them from clustering into aggregates large enough to plug fuel filters or injectors. Dispersants typically are used in the concentration range from 15 to 100 ppm.

Contaminant Control

This class of additives mainly is used to deal with housekeeping problems in distribution and storage systems.

Biocides

The high temperatures involved in refinery processing effectively sterilize diesel fuel. However, the fuel may quickly become contaminated if exposed to microorganisms present in air or water. These microorganisms include bacteria and fungi (yeasts and molds).

Because most microorganisms need free water to grow, biogrowth is usually concentrated at the fuel-water interface, when one exists. In addition to the fuel and water, they also need certain elemental nutrients in order to grow. Of these nutrients, phosphorous is the only one whose concentration might be low enough in a fuel system to limit biogrowth. Higher ambient temperatures also favor growth. Some organisms need air to grow (aerobic), while others only grow in the absence of air (anaerobic).

The time available for growth is also important. A few, or even a few thousand, organisms don’t pose a problem. Only when the colony has had time to grow much larger will it have produced enough acidic byproducts to accelerate tank corrosion or enough biomass (microbial slime) to plug filters. Although growth can occur in working fuel tanks, static tanks, where fuel is being stored for an extended period of time, are a much better growth environment when water is present.

Biocides can be used when microorganisms reach problem levels. The best choice is an additive that dissolves in both fuel and water to attack the microbes in both phases. Biocides typically are used in the concentration range from 200 to 600 ppm.

A biocide may not work if a heavy biofilm has accumulated on the surface of the tank or other equipment, because it may not be able to penetrate to the organisms living deep within the film. In such cases, the tank must be drained and mechanically cleaned.

Even if the biocide effectively stops biogrowth, it still may be necessary to remove the accumulated biomass to avoid filter plugging. Any water bottoms that contain biocides must be disposed of appropriately because biocides are toxic.

The best approach to microbial contamination is prevention. The most important preventative step is keeping the amount of water in a fuel storage tank as low as possible, preferably at zero.

Demulsifiers
Normally, hydrocarbons and water separate rapidly and cleanly. However, if the fuel contains polar compounds that behave like surfactants and if free water is present, the fuel and water can form an emulsion. Any operation which subjects the mixture to high shear forces (such as pumping the fuel) can stabilize the emulsion. Demulsifiers are surfactants that break up emulsions and allow the fuel and water to separate. Demulsifiers typically are used in the concentration range from 5 to 30 ppm.

Corrosion Inhibitors
Most petroleum pipes and tanks are made of steel and the most common type of corrosion is the formation of rust in the presence of water. Over time severe rusting can eat holes in steel walls, and create leaks. More immediately, the fuel is contaminated by rust particles, which can plug fuel filters or increase fuel pump and injector wear.

Corrosion inhibitors are compounds that attach to metal surfaces and form a protective barrier that prevents attack by corrosive agents. They typically are used in the concentration range from 5 to 15 ppm.

Red Dye in Diesel Fuel Sold in the U.S.

As stated in *Chapter 3 – Diesel Fuel and Air Quality*, the EPA and the IRS require the use of red dye in certain diesel fuel and for certain uses.

USE OF ADDITIVES

Additives may be added to diesel fuel at the refinery, during distribution, or after the fuel has left the terminal. During distribution, additives may be injected before pipeline transit (if the fuel is distributed by pipeline) or at the terminal.

Most pipelines carry multiple products, such as diesel, gasoline, and jet fuel. To avoid the possibility of diesel fuel additives intermixing with other products (particularly jet fuel) within the pipeline, additives must be added to the diesel fuel at the terminal after pipeline receipt. When the fuel leaves the terminal, its ownership generally transfers from the refiner or marketer to the customer (who may be a reseller [jobber] or the ultimate user). For this reason, additives added to the fuel after it leaves the terminal are called aftermarket additives.

This review discusses the many factors that determine the quality of diesel fuel. Given their number, it must be obvious that the quality of all diesel fuels is not the same. However, because fuel is the single largest operating expense for a diesel truck fleet, many users make their purchase decisions based on price alone.

Fuel marketers have a legal requirement to provide a product that meets all applicable specifications. Beyond that, reputable fuel suppliers ensure that the non-specification properties, such as stability and low-temperature operability, are suitable for the intended use.

The marketer has several options on how to achieve the desired properties: choice of crude oil, refinery processing, refinery blending, or the use of additives. The balance between refining actions and additive use is driven by economics. Because there are no legal requirements that diesel fuel contain additives, except red dye in high-sulfur and tax-exempt fuel, some refiners may use no additives at all and still provide a high-quality fuel.

There is no published information on the extent to which diesel additives are used in the marketplace. The following comments represent the authors' impression of common industry practice in the U.S.:

- Currently, because of the recent adoption of a lubricity specification, lubricity additive is the most widely used diesel additive nationwide all year round. Because of pipeline regulations in the U.S., lubricity additives are added at the terminals.
- Pour point reducers are widely used by refiners. However, their use is limited to fuel made in the wintertime and destined for regions with colder ambient temperatures.
- Some refiners add one or more additives to improve fuel stability, either as a regular practice or on an "as needed" basis. The transition to ultra-low sulfur diesel (15-ppm sulfur max), which is more stable, has significantly reduced the need for this type of additive.
- Some refiners use a cetane number improver, when the additive cost is less than the cost of processing, to increase the cetane number.
- Cloud point is the property used in the U.S. to measure the low-temperature operability of diesel fuel. Most refiners control cloud point by processing changes because cloud point reducing additives have historically been relatively ineffective.

- Antifoam additives are widely used in Europe and Asia to ensure that consumers can fill their cars and trucks without spilling fuel on their hands, clothing, and vehicles. There is less of a problem with fuel foaming in North America because of different fuel properties (lower distillation end point), vehicle tank designs, and fuel dispensing pumps. In addition, there are relatively few light-duty diesel vehicles (which tend to be more sensitive to fuel foaming).

California: A Special Case

Because of its unique diesel fuel regulations, California is a special case. California regulations restrict the aromatics content of diesel fuel in order to reduce emissions. The regulations can be met with either a low aromatics diesel (LAD), having less than 10 wt% aromatics, or with an alternative low aromatics diesel (ALAD) formulation that gives an equivalent reduction in emissions. Many of these ALAD formulations use cetane number improvers to help achieve the necessary emissions reduction. As a result, a significant percentage of the diesel fuel now sold in California contains some cetane number improver.[2]

Reducing diesel aromatic content to 10 wt% requires more severe hydrotreating than reducing sulfur content. As a result of this severe hydrotreating (which removes the molecules responsible for boundary lubrication), the lubricity of some LAD may be low, and some suppliers may treat the fuel with a lubricity additive. The ASTM D 975 diesel fuel specification requires a minimum level of lubricity for all diesel fuels. The lubricity specification states that all diesel fuels must have sufficient lubricity to produce a wear scar diameter no larger than 520 microns using the High Frequency Reciprocating Rig (HFRR, ASTM D 6079).

Distribution System Additization

When diesel fuel is distributed by pipeline, the pipeline operator may inject corrosion-inhibiting and/or drag-reducing additives.

Some refiners and petroleum marketers offer a premium diesel (see page 50), which can be created at the refinery by special blending and processing, or at the terminal by treating regular diesel with additives. From a practical point of view, most premium packages are produced at fuel terminals.

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[2] "Survey of Refining Operations and Product Quality," Final Report, 1996 American Petroleum Institute/National Petroleum Refiners Association (July 1997).

Refiners and marketers will often use a specially formulated blend of several additives, called an additive package, rather than a single additive. The additive package may contain:

- A detergent/dispersant
- Lubricity improver
- One or more stabilizing additives
- A cetane number improver
- A low-temperature operability additive (flow improver or pour point reducer)
- A conductivity additive
- A biocide
- A corrosion inhibitor

Each refiner or marketer is likely to use a different package of additives and a different treat rate. There are good reasons for this; many additives must be tailored to the fuel in which they will be used, and the requirements of the market vary from place to place.

Aftermarket Additives

It would be convenient for the user if a finished diesel fuel could satisfy all of his or her requirements without the use of supplemental additives. Although this is usually the case, some users require additional additives because the low-temperature conditions in their region are more severe than those for which the fuel was designed or because of other special circumstances. Other users feel that they will benefit from using a diesel fuel with enhanced properties compared to using regular diesel. Finally, there are users who regard the cost of an additive as cheap insurance for their large investment in equipment.

A large number of aftermarket additive products are available to meet these real or perceived needs. Some are aggressively marketed with testimonials and bold performance claims that seem “too good to be true.” As with any purchase, it is wise to remember the advice, *caveat emptor*, “let the buyer beware.”

It may be helpful to regard additives as medicine for fuel. Like medicine, they should be prescribed by an expert who has made an effort to diagnose the problem, as well as the underlying causes. Additives should be used in accordance with the recommendations of the engine manufacturer, and the instructions of the additive supplier. Sometimes, indiscriminant use of additives can do more harm than good because of unexpected interactions.

Appendix

SPECIFICATIONS FOR OTHER MID-DISTILLATE PRODUCTS

Included in this section are the ASTM specifications of other mid-distillate products that are similar to No. 1-D and No. 2-D diesel fuel. The detailed requirements are shown in Table 1 – ASTM D 396 *Fuel Oils*; Table 2 – ASTM D 2880 *Gas Turbine Fuel Oils*; Table 3 – ASTM D 1655 *Aviation Turbine Fuels*; and Table 4 – ASTM D 3699 *Kerosine*.

Please see ASTM D 396 for the complete set of requirements for No. 4 (light), No. 4, No. 5 (light), No. 5, and No. 6 fuel oils; and ASTM D 2880 for No. 3-GT and No. 4-GT gas turbine oils.

Table 1

ASTM D 396 – Detailed Requirements for Fuel Oils

Property	Test Methods	S500, S5000 No. 1	S500, S5000 No. 2
Flash Point, °C (°F), min	D 93 – Proc. A	38 (100)	38 (100)
Water and Sediment, % Vol, max	D 2709	0.05	0.05
Distillation – one of the following requirements shall be met:			
1. *Physical Distillation,* °C (°F)	D 86		
10% volume recovered, max		215 (420)	–
90% volume recovered, min		–	282 (540)
90% volume recovered, max		288 (550)	338 (640)
2. *Simulated Distillation,* °C (°F)	D 2887		
10% volume recovered, max		195 (380)	–
90% volume recovered, min		–	300 (570)
90% volume recovered, max		304 (580)	356 (670)
Kinematic Viscosity, mm^2/S at 40°C (104°F),	D 445		
min		1.3	1.9
max		2.1	3.4
Ramsbottom Carbon Residue, max, (% Mass on 10% Distillation Residue)	D 524	0.15	0.35
Sulfur, % mass, max	D 2622 D 129	0.05 0.50	0.05 0.50
Copper Strip Corrosion Rating, max, after 3 hours at 50°C	D 130	No. 3	No. 3
Density at 15°C, kg/m^3	D 1298		
min		–	–
max		850	876
Pour Point, °C (°F), max	D 97	-18 (0)	-6 (21)

Table 2

ASTM D 2880 – Detailed Requirements for Gas Turbine Fuel Oils at Time and Place of Custody Transfer to User

Property	Test Methods	No. 1-GT	No. 2-GT
Flash Point, °C (°F), min	D 93	38 (100)	38 (100)
Distillation Temperature, °C (°F) 90% Volume Recovered,	D 86		
min		–	282 (540)
max		288 (550)	338 (640)
Ramsbottom Carbon Residue, max (% mass on 10% Distillation Residue)	D 524	0.15	0.35
Kinematic Viscosity, mm^2/s at 40°C (104°F),			
min		1.3	1.9
max		2.4	4.1
Water and Sediment, % Vol, max	D 2709	0.05	0.05
Ash, % mass, max	D 482	0.01	0.01
Density at 15°C, kg/m^3, max	D 1298	850	876
Pour Point, °C (°F), max	D 97	-18 (0)	-6 (21)

Table 3

ASTM D 1655 – Detailed Requirements of Aviation Turbine

Property	Test Methods	Jet A or JetA-1
Composition		
Acidity, total mg KOH/g, max	D 3242	0.10
1. Aromatics, vol %, max	D 1319	25
2. Aromatics, vol %, max	D 6379	26.5
Sulfur, Mercaptan, mass %, max	D 3227	0.003
Sulfur, total mass %, max	D 1266, D 2622, D 4294, or D 5453	0.30
Volatility		
Distillation – one of the following requirements shall be met:		
1. Physical Distillation	D 86	
Distillation Temperature, °C (°F)		
10% recovered, max		205 (401)
50% recovered		Report
90% recovered		Report
Final Boiling Point, max		300 (572)
Distillation Residue, %, max		1.5
Distillation Loss, %, max		1.5

Table 3 (continued)

ASTM D 1655 – Detailed Requirements of Aviation Turbine Fuels

Property	Test Methods	Jet A or Jet A-1
2. Simulated Distillation	D 2887	
Distillation Temperature °C (°F)		
0% recovered, max		185 (365)
50% recovered, max		Report
90% recovered, max		Report
Final Boiling Point, max		340 (644)
Flash Point, °C (°F)	D 56 or D 3828	38 (100)
Density at 15 °C, kg/m^3	D 1298 or D 4052	775 to 840
Fluidity		
Freezing Point, °C (°F), max	D 5972, D 7153, D 7154, or D 2386	−40 (−40) Jet A −47 (53) Jet A-1
Viscosity at −20°C, mm^2/s, max	D 445	8.0
Combustion		
Net Heat of Combustion, MJ/kg, min	D 4529, D 3338, or D 4809	42.8
One of the following requirements shall be met:		
1. Smoke Point, mm,	D 1322	25
or		
2. Smoke Point, mm, and	D 1322	18
Naphthalenes, vol %, max	D 1840	3.0
Corrosion		
Copper Strip, 2 hours at 100°C (212°F), max	D 130	No. 1
Thermal Stability		
JFTOT (2.5 hours at control temperature of 260°C (500°F), min	D 3241	
Filter Pressure Drop, mm Hg, max		25
Tube deposits less than		3 No *Peacock* or *Abnormal* Color Deposits
Contaminants		
Existent Gum, mg/100 mL, max	D 381, IP 540	7
Microseparometer, Rating	D 3948	
Without Electrical Conductivity Additive, min		85
With Electrical Conductivity Additive, min		70
Additives		
Electrical Conductivity, pS/m	D 2624	Note 1

Note 1: If an electrical conductivity additive is used, the conductivity shall not exceed 600 pS/m at the point of use of the fuel. When electrical conductivity additive is specified by the purchaser, the conductivity shall be 50 to 600 pS/m under the conditions at the point of delivery.

Table 4

ASTM D 3699 – Detailed Requirements for Kerosine

Property	Test Methods	Limit
Flash Point, °C (°F), min	D 56	38 (100)
Distillation – one of the following requirements must be met:		
1. *Physical Distillation*	D 86	
Distillation Temperature, °C (°F)		
10% vol recovered, max		205 (401)
Final Boiling Point, max		300 (572)
2. *Simulated Distillation*	D 2887	
Distillation Temperature, °C (°F)		
10% vol recovered, max		185 (365)
Final Boiling Point, max		340 (644)
Kinematic Viscosity at 40°C, mm^2/s	D 445	
min		1.0
max		1.9
Sulfur, % mass	D 1266	
No. 1-K, max		0.04
No. 2-K, max		0.30
Mercaptan Sulfur, % mass, max	D 3227	0.003
Copper Strip Corrosion Rating, max 3 hours at 100°C (212°F)	D 130	No. 3
Freezing Point, °C (°F), max	D 2386	-30 (-22)
Burning Quality, min	D 187	Pass
Saybolt Color, min	D 156	+ 16

Questions and Answers

Is the color of diesel fuel an indication of its quality?

The color of a diesel fuel is not related to its quality. As long as the fuel meets specifications, it will perform well in your engine. The natural color of diesel fuels has traditionally varied from colorless to amber. As refinery processing of diesel fuel increased to remove sulfur, the color tends to get lighter and the diesel can change color. When it changes color, the diesel is typically light in tone and can be green, orange, or pink. Sometimes it might show a slight fluorescence when held up to light. Such a change in color does not affect the quality of the fuel.

What special precautions need to be taken with diesel fuel that must be stored for a long period of time?

While storage stability should not be a concern for the majority of diesel fuel users, those who store diesel fuel for a prolonged period, i.e., one year or longer, can take steps to maintain fuel integrity. The steps below provide increasing levels of protection:

1. Purchase clean, dry fuel from a reputable supplier and keep the stored fuel cool and dry. The presence of free water encourages the corrosion of metal storage tanks and provides the medium for microbiological growth.

2. Add an appropriate stabilizer that contains an antioxidant, biocide, and corrosion inhibitor.

3. Use a fuel quality management service to regularly test the fuel, and, as necessary, polish it – by filtration through portable filters – and add fresh stabilizer. This is common practice for nuclear power plants with backup diesel-powered generators.

4. Install a dedicated fuel quality management system that automatically tests and purifies the fuel and injects fresh stabilizer.

Do some diesel fuels lack lubricity?

Yes. Lubricity is a measure of the fuel's ability to prevent excessive wear when sliding and rotating parts in fuel pumps and injectors come in contact. The processing required to reduce sulfur to 15 ppm may remove naturally occurring lubricity agents in diesel fuel. To manage this change, ASTM International D 975 requires a wear scar no larger than 520 microns using the ASTM D 6079 *High Frequency Reciprocating Rig Test Method*. This specification provides sufficient fuel lubricity to protect equipment.

Will very low sulfur diesel fuels affect my fuel system seals?

The Clean Diesel Fuel Alliance, an industry group consisting of oil and gas producers, engine manufacturers, the American Petroleum Institute (API), and others, states that "engine and vehicle manufacturers are not anticipating that existing [diesel engine] owners will have to make changes to their equipment to operate [on] the new fuel.

A small number of vehicles may require preventative maintenance in the form of upgrading certain engine and fuel system seals that may not perform well in the transition to the new fuel and could leak. Studies of test fleets have indicated that fuel system leaks are not exclusive to a particular engine type, fuel type or geographic region. It is anticipated that only a small fraction of the vehicles will be affected."

A leak in your fuel system can be dangerous, potentially causing fires to occur if diesel fuel comes in contact with hot engine parts. It is recommended that you consult with your vehicle manufacturer for advice about maintaining or replacing the fuel system seals in your vehicle.

Please refer to our technical bulletin, *Fuel Leaks from Seals of Vehicles Using Ultra Low Sulfur Diesel*, for additional information. (http://www.chevron.com/products/prodserv/fuels/diesel/documents/elastomer_chevron_tb_2005Aug.pdf)

I accidentally mixed gasoline with my diesel fuel. What can I do?

One percent or less of gasoline will lower the flash point of a gasoline/diesel fuel blend below the specification minimum for diesel fuel. This will not affect the fuel's engine performance, but it will make the fuel more hazardous to handle. Larger amounts of gasoline will lower the viscosity and/or cetane number of the blend below the specification minimums for diesel fuel. These changes can degrade combustion and increase wear.

The best course of action is to recycle gasoline-contaminated diesel fuel back to your supplier. People ask if they can correct the problem by adding more diesel fuel to the blend. Usually the answer is no; the amount of additional diesel fuel needed to bring the flash point on test is impractically large. Those who try dilution should have the blend checked by a laboratory before use to be sure it meets specifications.

Does diesel fuel plug filters?

A plugged filter can be caused by several reasons. For example, if summer diesel is used during cold weather, low temperature can cause wax crystallization, which can lead to filter plugging. Dirt in the fuel or excessive microbial growth can also cause filter plugging. The latter are "housekeeping" issues and are not directly related to the fuel itself.

Under some circumstances, a fuel with poor thermal stability can plug a filter. When the fuel is exposed to the hot surfaces of the injectors, it forms particulates. If the fuel system is designed to return a significant proportion of the fuel to the fuel tank, the particulates are also returned. When the fuel is recycled, the fuel filter collects some of the particulates. Over time, particulate buildup plugs the filter. This problem has been observed for engines that were operating at high load and, therefore, engines that were operating at higher than average temperatures.

Has the energy content of diesel fuel changed?

In general, the processing required to reduce sulfur to 15 ppm also reduces the aromatics content and density of diesel fuel, resulting in a reduction in energy content (Btu/gal or kJ/liter).

The expected reduction in energy content is on the order of 1 percent and may affect fuel mileage.

What is the cetane number of diesel fuel?

In the U.S. the minimum is cetane number is 40. Some states have higher minimum cetane numbers. The European Union requires a minimum cetane number of 51.

How much No. 1-D diesel fuel must I add to No. 2-D diesel fuel to lower the cloud point for winter weather?

The cloud point of No. 2-D is lowered by about 3°F for every 10 percent volume of No. 1-D in the blend. Lowering the cloud point by 10°F requires the addition of more than 30 percent volume No. 1-D. It is important to ensure that the added No. 1-D has a compatible sulfur level.

What is the difference between No. 1-D diesel fuel and No. 2-D diesel fuel, and can they be used interchangeably?

Always check with the manufacturer about the fuel requirements of your engine. However, both No. 1-D and No. 2-D are intended for use in compression ignition engines. In fact, in cold weather, No. 1-D is blended into No. 2-D or used by itself.

Two of the biggest differences between the two fuels are heat content, and viscosity. Because No. 1-D is less dense than No. 2-D, its heat content (measured in Btu/Gal) will be a few percent lower leading to a similar reduction in fuel economy.

Can I get rid of my used engine oil by adding it to diesel fuel?

Adding used engine oil to diesel fuel used to be a common practice. However, it almost certainly results in a blend that does not meet diesel fuel specifications. One or more of these properties may be too high: 90 percent boiling point, sulfur content, ash, water and sediment, viscosity, and carbon residue. A diesel fuel/used oil blend may not be sold as diesel fuel and we recommend against using it as a diesel fuel.

In California, the addition of used engine oil to diesel fuel is a violation of hazardous waste regulations. Diesel fuel users in other areas who may consider this practice should check for any applicable regulations.

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Reformulated Diesel Fuel

Fuels and Energy Division Office of Mobile Sources
United States Environmental Protection Agency
401 M Street SW
Washington, D.C.
(202) 233-9000
http://www.epa.gov/omswww/

Biodiesel

U.S. DOE National Renewable Energy Laboratory,
http://www.nrel.gov/

Federal Regulations

Fuels and Energy Division Office of Mobile Sources
United States Environmental Protection Agency
Mail Code: 6406J
401 M Street SW
Washington, D.C.
(202) 233-9000
http://www.epa.gov/omswww/

Code of Federal Regulations,
Title 40 – Protection of Environment

- Part 51 – Requirements for Preparation, Adoption, and Submittal of Implementation Plans
  - Subpart S – Inspection/Maintenance Program Requirements
- Part 79 – Registration of Fuels and Fuel Additives
- Part 80 – Regulation of Fuels and Fuel Additives
- Part 85 – Control of Air Pollution From Motor Vehicles and Motor Vehicle Engines
- Part 86 – Control of Air Pollution From New and In-use Motor Vehicles and In-use Motor Vehicle Engines and Test Procedures

National Vehicles and Fuel Emission Laboratory
Office of Mobile Sources
United States Environmental Protection Agency
2565 Plymouth Road
Ann Arbor, Michigan 48105
(313) 668-4200

California Regulations

California Air Resources Board
P.O. Box 2815
Sacramento, CA 95814
(916) 322-2990
http://www.arb.ca.gov/

Questions?

Contact Chevron Fuels Technical Service
(510) 242-5357
Email: fueltek@chevron.com

Abbreviations

°API	degrees API, the unit of gravity in the API system
°C	degrees Celsius, the unit of temperature in the metric (SI) system
°F	degrees Fahrenheit, the unit of temperature in the U.S. customary system
% mass	percent by mass
% vol	percent by volume
AAM	Alliance of Automobile Manufacturers
ALAD	alternative low aromatics diesel
API	American Petroleum Institute
ASTM	ASTM International (formerly American Society for Testing and Materials)
ATDC	after Top Dead Center
BDC	bottom dead center; the position of the piston at the bottom of its stroke
bhp/bhp-hr	brake horsepower/brake horsepower per hour, a unit of measurement expressing the power available at the engine shaft
BTDC	before Top Dead Center
Btu	British thermal unit
CAD	crank angle degrees
CARB	California Air Resources Board
CEN	European Committee for Standardization
CFPP	cold filter plugging point
CFR	Cooperative Fuel Research
CO	carbon monoxide
CO_2	carbon dioxide
CRC	Coordinating Research Council
cSt	Centistoke
CU	conductivity unit
DCN	derived cetane number
DI	direct-injection
DOE	U.S. Department of Energy
DTBP	di-tertiary butyl peroxide, a cetane number improver
ECU	electronic control unit
EHN	2-ethylhexylnitrate, a cetane number improver
EGR	exhaust gas recirculation
EMA	Engine Manufacturers Association
EPA	U.S. Environmental Protection Agency
FAME	fatty acid methyl esters
FCC	fluid catalytic cracking
g	gram, a metric unit that is one thousandth of a kilogram
g/bhp-hr	grams per brake-horsepower hour
g/cm^3	grams per cubic centimeter, a measurement of density
GTL	gas-to-liquid
HC	hydrocarbon
HFRR	high-frequency reciprocating rig; device for measuring fuel lubricity
IARC	International Agency for Research on Cancer
ICP	inductivity coupled plasma
ID	ignition delay
IDI	indirect-injection
IP	Institute of Petroleum
IMO	International Maritime Organization
IQT	ignition quality tester
IRS	Internal Revenue Service
ISO	International Standards Organization
kg/m^3	kilogram per cubic meter, an SI measurement of density
kPa	kilo Pascal: a unit of pressure in the metric (SI) system
kW/kW-hr	kilowatt/kilowatt-hour, a measurement of power

LAD	low aromatics diesel
LCO	light cycle oil
LTFT	low-temperature flow test
LPG	liquefied petroleum gas
mg/L	milligrams per liter
MJ/kg	mega joules per kilogram, a measurement of energy density
mm^2/s	millimeter squared per second; a unit of viscosity
MPa	mega Pascal: a unit of pressure in the metric (SI) system
N_2	diatomic nitrogen
nm	nanometer, a measurement of length
NAAQS	National Ambient Air Quality Standard
NCWM	National Conference on Weights and Measures
NIOSH	National Institute of Occupational Safety and Health
NMHC	non-methane hydrocarbons
NO	nitric oxide
NO_2	nitrogen dioxide
O_3	ozone
NO_x	nitrogen oxides (or oxides of nitrogen); NO + NO_2
PM	particulate matter
$PM_{2.5}$	particulate matter whose particle size is less than or equal to 2.5 microns
PM_{10}	particulate matter whose particle size is less than or equal to 10 microns
PAH	polycyclic aromatic hydrocarbon
PNA	polynuclear aromatic hydrocarbon
POM	polycyclic organic matter
ppm	parts per million
ptb	pounds per thousand barrels
RD	relative density
resid	Residual left after distillation; the heavier ends of the barrel
rpm	revolutions per minute
S15	15 ppm sulfur diesel fuel
S500	500 ppm sulfur diesel fuel
S5000	5000 ppm sulfur diesel fuel
SAE	SAE International (formerly Society of Automotive Engineers)
SCR	selective catalytic reduction
SECA	Sulfur Emissions and Control Areas
SIP	State Implementation Plan
SLBOCLE	scuffing load ball-on-cylinder lubricity evaluator
SO	sulfur oxide
SO_2	sulfur dioxide
SO_x	sulfur oxides; SO + SO_2
TDC	top dead center; the position of the piston at the top of its stroke
T_{95}	temperature at which 95 percent of fuel has distilled in test method ASTM D 86
ULSD	ultra-low sulfur diesel
UV light	ultraviolet light
VGO	vacuum gas oil
VOC	volatile organic compound
WSD	wear scar diameter

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