GASOLINE AND OTHER MOTOR FUELS

1. Introduction

Gasoline and other motor fuels comprise the largest single use of energy in the United States, and in 2002 accounted for 22% of all energy usage (1). The cost of this energy has been and is expected to continue to be a primary factor in the national economy. Moreover, the fraction of resources from which these fuels come that is provided by foreign sources is a matter of political concern (see FUEL RESOURCES). The fraction of total crude oil produced domestically shrunk from 75% in 1970 to 39% in 2002 (2) and is predicted to continue to drop (see NOMENCLATURE IN THE PETROLEUM INDUSTRY). Imported products also continue to grow. In 2002, the United States imported 130 10^6 L/day of gasoline and gasoline components. In the 1970s, two Organization of Petroleum Exporting Countries (OPEC) embargoes resulted in rapid increases in the price of crude oil and therefore motor fuels. These increases triggered programs designed to develop alternative sources of fuels such as coal (qv), oil shale (qv), and natural gas (see FUELS, SYNTHETIC, GASEOUS FUELS; GAS NATURAL). In 2001, as a result of lower price volatility and improved energy efficiencies, the inflation adjusted cost of driving an average passenger car is about 40% lower than it was in 1960 (3). Today, alternative transportation fuels are being considered as replacements for traditional petroleum based fuels based on their perceived potential to improve the security of energy supply and to reduce emissions of greenhouse gases. Among alternative fuels under consideration are hydrogen, natural gas and biofuels such as ethanol and esterified edible oils. (see also AIR POLLUTION; EXHAUST CONTROL, AUTOMOTIVE).

1.1. General Aspects of Manufacture of Motor Fuels.

All motor fuel in the United States is manufactured by private companies. Many of these are vertically integrated. That is, the same company finds the crude oil or buys it from a producing government, refines it into finished products, and then sells these products to independent retailers who specialize in that company's blended products or sells them at company operated service stations. There are also a significant number of companies that participate in only some aspects of the business cycle such as refining or marketing.

Four groups are involved in the production or use of motor fuels in the United States: (*1*) manufacturers of the vehicles; (*2*) manufacturers and/or marketers of the fuels; (*3*) purchasers and users of fuels and vehicles; and (*4*) federal, state, and local regulatory agencies (qv). Each has a different role.

Vehicle manufacturers must build cars and trucks that operate well on available fuels. They also specify the fuel requirements of their vehicles. Fuel marketers must produce fuels that operate in both new and old vehicles. The consumer, the purchaser of the fuel and the vehicle, wants the fuel to be affordable, readily available, and able to provide a high level of performance. Regulators check that fuels are labeled properly and meaningfully and that no unwarranted claims are made. They also regulate emissions from vehicles and set fuel specifications based on environmental considerations.

Appropriate specifications are set when the vehicle and the fuel are viewed as a system, and when all four groups, or stakeholders, work together to define cost effective and efficient solutions that satisfy the needs of all stakeholders. The American Society of Testing and Materials (ASTM), now known as ASTM International was founded in 1902 to promote just such a process. ASTM Committee D-2 provides a forum for regulators, vehicle manufacturers, fuel producers, and consumers to develop and recommend nonbinding standards for petroleum products. Among the types of ASTM standards are Specifications and Test methods. Specifications define a precise set of requirements to be satisfied by a material. Test methods define procedures for measuring qualities and characteristics of a material. Specifications for gasoline are contained in ASTM D 4814 (4) and for automotive diesel fuel in ASTM D 975 (5). These standards are updated periodically.

ASTM committees must be balanced in that the number of voting producers must not be greater than the number of voting nonproducers. For petroleum products, nonproducers are regulators, consumers, and equipment manufacturers. Committee chairs must be nonproducers. Although standards must be approved by a majority, all negative votes must be carefully considered and a response made. In practice, because all issues are fully discussed and the discussions are based on hard data, very few negative votes are cast when standards are submitted for final approval. Although ASTM specifications do not have the force of law, many states have adopted them as state regulation, thus forcing a minimum quality level in the field.

ASTM specifications cover those aspects of fuel properties that ensure good performance in gasoline and diesel powered vehicles. Other fuel properties are controlled for environmental reasons. These environmental related specifications are set by government agencies on the national (Environmental Protection Agency), state (eg, California Air Resources Board) and even local levels.

The legal authority to set specifications based on environmental needs derives from the Clean Air Act, which was last amended in 1990. Fuel composition regulations may be set to provide direct benefits to the environment (eg, lower vapor pressure) or to allow emission control systems to operate properly (eg, lead free gasoline). Environmental regulations are generally developed in an open public process where all stakeholders have an opportunity to comment and provide input. Government agencies, which make the final decision, must show that their decisions protect the public health and welfare, are cost-effective and fair to all parties.

In June, 1998, a coalition of automotive manufacturers attempted to circumvent the traditional standard setting mechanism by publishing the World Wide Fuel Charter (WWFC). Four sets of specifications were defined for gasoline and diesel, based on four levels of vehicle technology and environmental regulations. Predictably, the specifications reflected the view of the automotive manufacturers and no members of the petroleum industry have adopted the WWFC. Regulatory agencies have not adopted the WWFC either, preferring to work within existing groups and procedures.

2. Gasoline

Gasoline, the preferred fuel for the Otto engine, evolved from an unwanted by-product to an indispensable mainstay of modern life in only a few short years. In 1900, gasoline was little more than a disposal problem for the infant petroleum industry in the production of stove and lamp oils, lubricating oils, and greases. The first prototype four-stroke, internal combustion, spark-ignited engine was built by Nicolaus Otto in 1876 in Germany. This engine, which ran on gasoline, provided enormous advantages over earlier internal combustion designs in terms of weight, power, and efficiency. By 1890, almost 50,000 of these engines had been sold. As the popularity of these engines grew at an exponential rate, the demand for gasoline grew accordingly. Gasoline demand grew by a factor of five between 1907 and 1915.

Figure 1 shows the growth in gasoline demand in the United States since 1950 (6). Demand is largely determined by the growth in the number of cars, the kilometers of paved roads available for driving, population, and economic growth. Figure 1 also shows the number of passenger vehicles and the average yearly distance driven per vehicle (7). Most Americans drive to work, to shop, and for recreation. In 2002, American consumers burned 503×10^9L of gasoline. The average passenger vehicle is driven about 19,000 km/yr, up from about 15,000 km/yr in 1950. Despite stated goals of reducing the number of kilometers that people drive to work through increased use of mass transit and car-pooling, the public's preference for personal driving has remained strong.

A primary factor in moderating the demand for gasoline has been the dramatic improvement in automotive fuel economy from the mid-1970s through the mid-1980s. Figure 2 shows the trend in fuel economy for new cars since 1955 and for light duty trucks from 1980 (8). Improvement is the result of governmental regulations that were a direct outcome of the oil shortages of the 1970s. Average

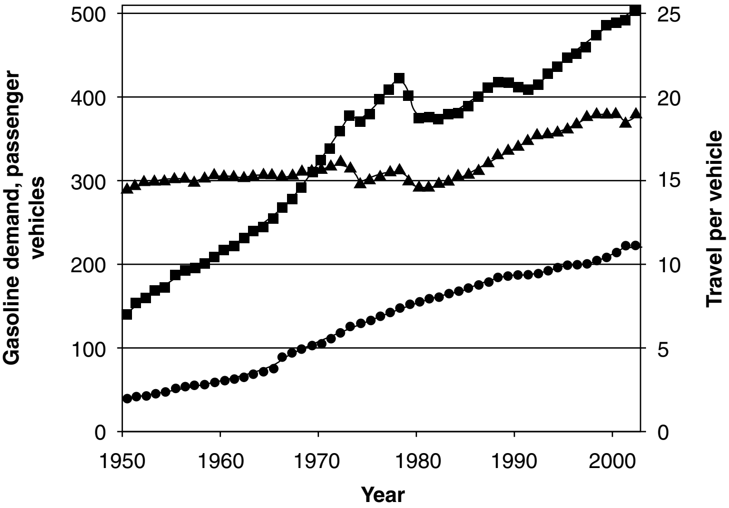

Fig. 1. Growth in annual gasoline demand, in GL/yr; millions of passenger cars; and travel per vehicle, in km/yr. —●— Passenger vehicles, × 10^6, —■— gasoline demand, GL/yr, and —▲— travel per vehicle, 1000 km/yr.

fuel economy has remained virtually constant since the mid-1980s, as no new regulations have been imposed. This clearly shows that the current cost structure of gasoline is not a significant impediment to people's desire to drive, and that, in general, the consuming pubic would rather have larger, more powerful family vehicles than smaller more efficient ones.

Energy outlooks are developed annually by the Department of Energy. In their most recent forecast for the years 2002–2025, energy demand for light duty vehicles is projected to grow about 1.9% per year between 2002 and 2025,

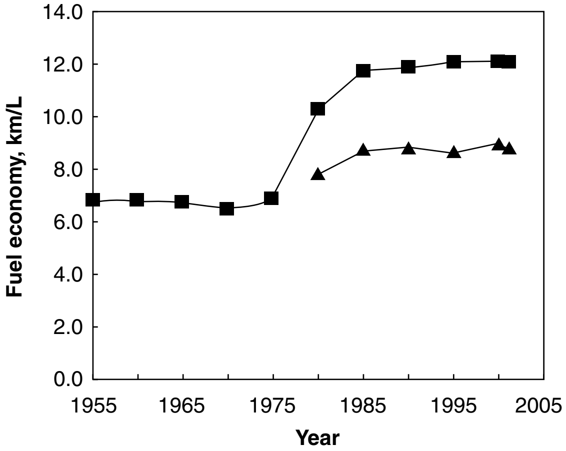

Fig. 2. Fleet average fuel economy for new cars and light duty trucks. —■— Passenger cars —▲— light trucks.

1.9% per year for light commercial trucks and 2.2% per year for freight trucks (9). These projections include growth in travel and modest improvements in fuel economy. The recent trend of using technology to improve performance rather than efficiency will continue; average horsepower is projected to grow by 24% while fuel economy will improve by only 6%. It is expected that by 2025, 2.1% of light duty vehicles will be fueled by alternative fuels. It should be recognized that these projections are sensitive to many factors, including overall economic growth and fuel costs.

2.1. Requirements of Good Gasoline.

To satisfy high performance automotive engines, gasoline must meet exacting specifications, some of which are varied according to location and based on temperatures or altitudes. The fuel must evaporate easily and burn completely when the spark plug fires in each cylinder. Early detonation of the fuel in the cylinder can cause destructive engine knock. The fuel must be chemically stable. It should not form gums or other polymeric deposit precursors. There should be no particulate contaminants or entrained water. Contaminants must be prevented from the point of manufacture in the refinery all the way through the distribution system until the fuel is metered from the vehicle tank into the engine.

Octane. Octane is probably the single most recognized measure of gasoline quality. The octane value of gasolines are posted on service station dispensers, and most drivers recognize a fuel in which the octane is too low. Broadly speaking, octane is a measure of the combustion characteristics of gasoline. In an Otto cycle engine, gasoline vapor in the combustion chamber must start to burn only when the spark plug ignites after the charge has been compressed. Then it must burn with a well-defined flame front that travels all the way across the combustion chamber. Low octane gasoline has a tendency to preignite. As the flame front sweeps across the combustion chamber, the unburned portion of the fuel (end gas) heats up under rapidly rising temperature and pressure conditions. The fuel–air mixture undergoes chemical reactions that may cause it to autoignite and detonate the entire remaining mixture. Instead of being pushed down smoothly on the power stroke, the piston is given a hard instantaneous rap to which it cannot respond because of the large mechanical inertia present in the crankshaft and other pistons. This rapid energy release causes pressure fluctuations in the cylinder which result in a loud metallic noise commonly called knock. In addition to producing an objectionable sound, knock can reduce the amount of useful work that is extracted from the engine. Power is dissipated in the pressure waves, and increased heat is radiated to the cylinder walls and into the cooling water. Under extreme conditions of prolonged knock, overheating and even engine damage can occur. The damage is typically caused by catastrophic melting of piston crowns or head gaskets.

Knock is caused by unwanted chemical reactions in the combustion chamber. These reactions are a function of the specific chemical species which make up the fuel and the environmental conditions to which the fuel is subjected during the compression and power stroke in the engine. Therefore, both the chemical makeup of the fuel and the engine design parameters must be considered when trying to understand knock.

Chemical Factors. Because knock is caused by chemical reactions in the engine, it is reasonable to assume that chemical structure plays an important

Table 1. **Chemical Factors Affecting Knock**

	Change in knocking tendency	
Change in chemical structure	Increase	Decrease
longer paraffin chains	x	
isomerizing normal paraffins		x
aromatizing normal paraffins		x
alkylating aromatics		x
saturating aromatic rings	x	

role in determining the resistance of a particular compound to knock. Reactions that produce knock are generally free-radical chain-type reactions which are different from those that occur in the body of the flame; the former occur at lower temperatures and are called cool flame reactions. Peroxy and hydroperoxy radicals play important roles in the knock process. A number of good reviews have discussed the details of the chemical mechanisms (10). Ignition delay (tau) has also been used for description of the chemical tendency to knock (11). The chemical factors affecting knock are shown in Table 1.

A lengthy and systematic investigation into the cause and prevention of knock, culminated in the use of lead alkyl compounds such as tetraethyllead [78-00-2] (TEL) to decrease the knocking tendency of fuels dramatically. Lead alkyls function as antiknocks by decomposing in the combustion process to form lead oxides which terminate the free-radical chain mechanisms leading to knock. The problem with lead additives is the presence of lead in the exhaust and the consequent potential health effects on the population, especially children, living near roadways.

Lead also poisons the noble metal catalysts used on all gasoline powered motor vehicles sold in the United States today. In 1974, gasoline marketers started to sell unleaded gasoline and lead was totally banned by EPA in 1995 except for use in aviation gasoline and racing fuels. Today, lead is used widely only in certain countries in Africa and plans are in place to stop even that small use.

In 1957, Ethyl Corp. announced a new antiknock compound, methylcyclopentadienylmanganese tricarbonyl [12108-13-3] (MMT, trademark of Ethyl Corp.). MMT is almost as effective as lead on a per gram of metal basis, but because manganese was more expensive than lead, MMT was not widely used until limits were placed on the lead content of gasoline. The Clean Air Amendments of 1990 banned the use of MMT in reformulated gasoline (gasoline blended to reduce emissions). Automotive manufacturers generally oppose the use of MMT in new vehicles because they claim that the additive increases emissions by affecting catalysts, control systems and spark plugs (12). Although EPA allows MMT use in conventional gasoline, little or none is used in the United States today. It has been widely used in Canada although its use there is also being challenged by automotive manufacturers.

Vehicle Factors. Because knock is a chemical reaction, it is sensitive to temperature and reaction time. Temperature can, in turn, be affected either by external factors such as the wall temperature or by the amount of heat released in the combustion process itself, which is directly related to the density of the fuel–air mixture. A vehicle factor which increases charge density, combustion chamber temperatures, or available reaction time promotes the tendency to knock. Engine operating and design factors which affect the tendency to produce knocking are

Increased Knock	Decreased Knock
Higher compression ratio	Increased turbulence
Advanced spark schedule	Exhaust gas recycle
Higher coolant temperature	Cooled air charge
Turbocharging or supercharging	High altitudes
Combustion chamber deposits	High humidity
Engine loading	

Generally, anything which increases the efficiency or power output of the engine increases the tendency to knock. Higher compression ratio increases the initial temperature of the fuel–air charge and therefore the peak combustion temperatures. Combustion chamber deposits are highly insulating and reduce the amount of heat rejected to the coolant, thereby increasing combustion chamber temperatures. Advancing the time in the cycle at which the spark plug fires provides more time for the end gas to undergo preknock reactions. One of the easiest fixes for a knocking engine is to retard the spark timing. The engine loses a little power but the knocking can almost always be eliminated. In a similar manner, designing the combustion chamber to promote shorter burn times can effectively reduce knocking tendencies. Putting the spark plug near the center of the combustion chamber is one way. Another is to promote turbulence during burning thus increasing flame speed.

Ambient conditions can also affect knocking tendency. At high altitudes, air density is lower and the combustion of the fuel air charge generates less heat. High humidity dilutes the oxygen with water vapor and also interferes with some of the knock reactions leading to lower knocking tendencies.

Measuring Octane. Two different values need to be considered when discussing octane measurements. One is the knocking tendency of the fuel, called the fuel octane number. The other is the knocking tendency of the vehicle, called octane number requirement.

It is impractical to measure a fuel's octane number in a full-sized vehicle. Thus laboratory techniques have been developed through ASTM to measure these numbers in well-defined engines. The standard knock engine is a single cylinder cooperative fuels research (CFR) engine. This engine has a compression ratio which can be varied between 3 and 30. It also has four carburetor bowls so that reference and test fuels can be switched easily. It is equipped with a magneto-restrictive type detonation sensor that measures the rapid change in pressure characteristic of knock. Two primary reference fuels (PRFs) have been defined: 2,2,4-trimethylpentane [540-84-1], commonly referred to as isooctane, has an octane number of 100 and *n*-heptane [142-82-5] has an octane

Table 2. **Octane Test Operating Conditions**

Condition	Research octane no. (ASTM D 2699)	Motor octane no. (ASTM D 2700)
engine speed, RPM	600	900
inlet air temperature, °C	51.7	38
mixture temperature, °C		149
spark advance, °BTDC[a]	13	14–26

[a] Spark advance for Motor method is a function of compression ratio. BTDC = before top dead center.

number of zero. Octane numbers of primary reference fuels between zero and 100 are formed by volumetric mixtures of isooctane and *n*-heptane. For example, a 50:50 mixture of the two has an octane number of 50. Primary reference fuels for measuring octane numbers above 100 contain specified amounts of tetraethyllead. For instance, isooctane containing 0.238 g TEL/L has a defined octane number of 108.

The octane value of an unknown fuel sample is determined by comparing its knocking tendency to various primary reference fuels. Its measured octane is equal to the octane of the PRF which has the same knocking intensity. Knock intensity is controlled to an average value by varying the compression ratio of the CFR engine. In practice, the exact value of a fuel's octane number is determined to the nearest 0.1 octane number by interpolation from two PRFs that are no more than two octane numbers apart.

The CFR engine is operated at two conditions to simulate typical on-road driving conditions. The less severe condition measures research octane number (RON); the more severe one measures motor octane number (MON). Table 2 summarizes the operating conditions for each test.

The difference between RON and MON for a particular fuel is called the sensitivity. By definition, the RON and MON of the primary reference fuels are the same and the sensitivity is zero. For all other fuels, the sensitivity is almost always greater than zero. Generally, paraffins have low sensitivities whereas olefins and aromatics have sensitivities ranging up to 10 and higher.

The octane numbers of many pure compounds have been measured and reported in the literature. Probably the most comprehensive project was carried out under the auspices of the American Petroleum Institute (13). Table 3 lists RON and MON values for a number of representative compounds. Some aromatic compounds cannot be tested neat in the knock engine, so these are evaluated at levels of 20%, and the equivalent octane number is calculated. The values for oxygenates in Table 2 have been reported elsewhere (14).

These two test methods and the octane numbers of the fuels measured are ultimately used to evaluate the performance of vehicles. The two methods provide useful information about how fuels perform in cars. The RON corresponds to light load, low speed conditions, whereas the MON corresponds to heavier loads, and high speed severe driving conditions.

The octane number requirement (ONR) of a car is the octane number which causes barely audible, ie, trace knock when driven by a trained rater. The Coordinating Research Council (CRC), a research organization funded jointly by the

Table 3. **Octane Numbers of Pure Compounds**

Compound	Research O.N.	Motor O.N.
paraffins		
n-pentane	61.8	63.2
n-hexane	24.8	26.0
n-heptane	0	0
2-methylbutane	92.3	90.3
2-methylpentane	73.4	73.5
2-methylhexane	42.4	46.4
olefins		
2-methyl2-butene	97.3	85.5
1-pentene	90.9	77.1
1-hexene	76.4	63.4
1-heptene	54.5	50.7
aromatics[a]		
toluene	124	112
o-xylene	120	102
ethylbenzene	124	107
propylbenzene	127	129
oxygenates		
ethanol	130	96
methyl *tert*-butyl ether (MTBE)	118	100
ethyl *tert*-butyl ether (ETBE)	118	102
methyl *tert*-amyl ether (TAME)	111	98

[a] Aromatics were measured in a 20% blend with a 60/40 mixture of 2,2,4-trimethylpentane and n-heptane.

American Petroleum Institute (API) and six members of the automotive industry (General Motors, Ford, Daimler-Chrysler, Toyota, Volkswagon and Honda), has defined test procedures for measuring ONR. Each car is driven under a set of light and heavy accelerations until the most sensitive driving mode is determined. Then a series of fuels is run in the car until trace knock is determined.

Auto manufacturers have developed knock detecting and limiting devices called knock sensors which are installed in most engines today. The sensor is a piezoelectric crystal which is tuned to the natural frequency of engine knock sound (see SENSORS). When knock is detected, a signal is sent to the on-board computer which retards the spark timing. In this way, knocking noise is eliminated until the maximum spark retard is reached. The tradeoff, however, is reduced power. Full throttle acceleration times can be increased by up to 10% when these cars use low octane fuel. Measuring octane number requirements in cars with knock sensors involves either determining when octane is sensed and spark retard is initiated, or sensing when the maximum level of retard has been reached. CRC has defined a test procedure for measuring the octane response of cars equipped with knock sensors (15).

It has long been known that the design of a car affects the way in which it responds to RON and MON. The response of a car to RON and MON can be characterized by a parameter called severity, which is a measure of its relative response to RON and MON. In the 1930s, most cars responded only to RON. That is, it did not really matter what the MON of a fuel was. As long as the RON was above a minimum value, the car would not knock. Cars of the 1990s generally have a severity of about 1, meaning that a 1 number change in RON can be offset by a corresponding and opposite change in MON to provide equivalent knocking protection. Octane numbers which are posted on gasoline dispensers in all states show the antiknock index which is the average of the RON and MON values of the gasoline being sold. Recent data suggest that modern cars respond mostly to RON and that consideration should be given to changing the way that octane is posted on gasoline dispensers (16,17).

In designing engines, automotive manufacturers must decide what kind of fuel that engine should use, from low to high octane. Compression ratio is the primary determining factor in a vehicle's octane requirements. High performance, high compression ratio engines need high octane or premium fuel. It is also known that the octane requirement of a vehicle increases as a vehicle ages. This phenomena, known as octane requirement increase (ORI), is caused by the buildup of fuel and lubricant based deposits in the combustion chamber. These deposits are highly insulating and increase the combustion wall temperature, thereby increasing the tendency to knock. Generally, ORI reaches an equilibrium value of 6–9 octane numbers over the first 24–32,000 kilometers of operation, although higher increases are not uncommon. In some cases, as cars age and start to burn more oil, octane requirements can increase again.

Over the years, engine compression ratios have undergone a number of changes. These increased rapidly through the 1950s and 1960s. The advent of unleaded gasoline and the demise of lead as a cheap source of octane, brought about a drop in fuel octane numbers and compression ratios. In the early 1980s, both compression ratios and average octane numbers requirements increased as a result of customer demand for more powerful cars.

The particular fuel octane number which a gasoline marketer chooses to produce and sell is determined by a number of factors including the cost of producing the various levels of octane, the number of customers requiring the various octane levels, and competitive offerings. Determining customer requirements is the most difficult. The surveys conducted by CRC measure vehicle ONR using trained raters. Trained raters are much more sensitive to knocking noise than the average customer. Consequently, octane requirements percieved by customers are generally lower than trained raters. This customer/rater delta has been the subject of a number of studies (18,19) and the average difference has been estimated to be between 3–5 octane numbers. Typically, a marketer decides that the premium grade should satisfy a certain fraction of customers, usually well over 90%. The octane values for the regular and/or intermediate grades are determined in a similar manner.

The optimum level of gasoline octane is a complex function of a number of factors involving the customer as well as the automotive and petroleum industries. Increasing octane values may require significant investment and higher operating costs on the part of the oil industry that could raise the price of gasoline to the consumer. On the other hand, vehicle manufacturers could take advantage of the availability of higher octane gasolines by raising the compression ratios of their engines which could in turn increase fuel economy due to higher thermal efficiency. Higher compression ratio engines may cost more to build, but the consumer would save in fuel costs over the life of the car.

Volatility. The properties of a gasoline which control its ability to evaporate are critical to good operation of a vehicle. In an Otto cycle engine, the fuel must be in the vapor state for combustion to take place. The volatility or vaporization characteristics of a gasoline are defined by three ASTM tests: Reid vapor pressure (RVP), the distillation curve, and the vapor/liquid ratio (V/L) at a given temperature, ASTM D 4953, D 86, and D 2533, respectively. These three tests are sufficient to describe the volatility related characteristics of gasoline and predict its driveability performance. Moreover, these are the specifications that industry and government use to define volatility characteristics. Proper choice of these parameters ensures that cars operate well under all ambient conditions.

RVP is a vapor pressure measurement at a fixed air/liquid ratio of 4 and a temperature of 38°C. ASTM has defined a number of tests which can be used to measure RVP: D 4953, D 5190, D 5191 and D 5482.

The distillation (qv) test, D 86, is a batch distillation using a specified heating rate. A 100-mL sample is distilled and the vapor temperatures at which various percentages of the sample have condensed are recorded. The data are reported as the temperature at which 10, 20, 30%, etc, of the sample has been evaporated. The amount of heavy material which does not evaporate is measured at the end of the test and the amount of light material which was not condensed is calculated by difference from the total condensate and the residue. The D 86 test approximates a one-plate distillation with limited recycle. It has been compared to the kind of distillation the gasoline undergoes in a carburetor and intake manifold. For the more detailed description of the volatility characteristics needed to design and run a refinery there are other tools which can be used to generate true boiling point (TBP) curves. TBP are essentially distillation curves run at high efficiency and reflux. One method uses a glass distillation column with 15 theoretical plates and a reflux ratio of 5. Another uses a gas chromatography technique to identify most or all of the individual compounds in the sample and then uses a computer-based chemical library to mathematically construct a distillation curve using known or estimated vapor pressures, fugacities, etc.

Distillation data may be expressed in two ways: the percent evaporated at a given temperature ($Exxx$); or the temperature for a given percent evaporation (T_{yy}). Because $Exxx$ values blend linearly, these are generally preferred by refiners and blenders. Gasoline performance specifications have been reported in both ways. ASTM specifications generally prefer the T_{yy} format.

The vapor/liquid ratio tests measure the amount of vapor formed from a given volume of liquid at a given temperature at atmospheric pressure. A common measure used in specifying gasoline is the temperature at which the vapor/liquid ratio is 20 ($\mathrm{T}_{\mathrm{V/L}=20}$). Although V/L can be measured experimentally, it is a difficult and time consuming test to carry out, and techniques have been developed to calculate it from RVP and D 86 values.

When designing fuel volatility targets, gasoline blenders must strike a balance between various driveability performance characteristics. Driveability refers to the ability of a car to start easily, accelerate and idle smoothly, and respond to changes in throttle position as expected. Too much volatility can cause as many problems as too little volatility. Targets must be matched to local ambient temperature conditions. As for other performance features, a good match between vehicle and fuel design is important to proper performance. Volatility requirements, like octane, are a strong function of vehicle design. A great deal of data on the volatility requirements of new cars is collected in cooperative programs run by CRC. Trained raters drive cars under strictly controlled conditions and evaluate the driveability performance on a range of fuels. Customers are generally less sensitive to problems than the raters. Each company decides which level of protection to provide. ASTM also uses these data to set target levels for the various fuel parameters.

Startability. In order to achieve combustion in an Otto cycle engine, the air/fuel ratio in the combustion chamber must be near the stoichiometric ratio. Unfortunately, when the engine is first started, the walls of the combustion chamber and the intake manifold are not hot enough to vaporize much fuel. Therefore, the vehicle is designed to meter extra fuel and less air to the engine upon start up so that there is adequate vapor in the engine to support combustion. From the fuel's perspective, a fuel which is easily vaporized and which contains a large percentage of light compounds such as butane is desirable to achieve good starting. The ability of a fuel to achieve good starting can be correlated with RVP and a measure of the front end of the distillation curve, either E70 or T_{10}. Usually, minimum levels of RVP such as 60 kPa (0.6 bar) and E70 minimum of 10% (or a T_{10} maximum of 60°C) are satisfactory for good startability in most winter locations (20). Obviously, fuel specifications change with ambient temperatures. At higher temperatures, lower RVP and front-end volatilities are adequate to provide good starting characteristics.

Vapor Lock. At the other end of the spectrum from starting is vapor lock, a problem of too much volatility. Vapor lock occurs when too much of the fuel evaporates and either starves the engine for fuel or provides too much fuel to the engine. It occurs on days that are warmer than usual and when the car has reached full operating temperatures. A typical situation would be when a car is stuck in heavy traffic; the engine reaches high temperatures and the fuel reaches its boiling point. Most cars today are fuel injected, have fuel pumps located in the tank and fuel lines which are under positive pressure. They are therefore less prone to vapor lock than older carbureted vehicles.

Vehicle manufacturers minimize vapor lock by keeping the fuel system cool and under positive pressure. Fuel manufacturers minimize the problems by seasonal volatility blending. As might be expected, the front end of the gasoline controls vapor lock. The temperature to obtain a V/L ratio of 20 is referred to in ASTM D 4814 as a way to control the vapor locking tendencies of gasoline.

Warm-Up. Warm-up refers to that period of operation beginning immediately after the car has started and continuing until the engine has reached normal operating temperatures, usually after 10 minutes or so of operation. During this period, the vehicle designer wants to get the vehicle equivalence ratio to stoichiometric as soon as possible to minimize emissions. On the other hand, if the mixture is leaned out too soon, the car experiences poor driveability during the warm-up period. Fuel system design is critical during this period. With older, single point fuel metering systems such as carburetors and throttle body injectors, there is generally liquid fuel on the walls of the intake manifold during warm-up. If this liquid only reaches the cylinders in bursts the vehicle may experience unwanted surges. Multipoint fuel injectors minimize many of these problems but makes the scheduling of the fuel pulses critical.

Manufacturers use powerful on-board computers to implement sophisticated and complex algorithms to control operation of fuel injectors during this critical period.

From the fuel's perspective, the middle of the distillation curve plays the largest role in achieving good warm-up performance. Under the typical vehicle operating regime, the front end of the fuel totally evaporates. The back end of the fuel, containing the heaviest molecules, has trouble evaporating at this point. The molecules boiling between about 100 and 150°C are the most important. Here again, the actual levels required are a strong function of ambient temperature. The critical periods are usually the Spring and Fall, when temperatures are between 0 and 15°C. At very cold temperatures, the RVP and front-end volatility are so high that there is adequate fuel vaporization. Also, because cold weather emission control has not been a principal concern, vehicles can be calibrated to maintain rich air/fuel ratios longer than in warmer weather. Similarly, in hot weather, the engine heats up faster and maldistribution is not as much of a problem.

The most common expression for controlling driveability is known as the driveability index (DI), which has the form:

$$\mathrm{DI} = 1.5^{*}T_{10} + 3^{*}T_{50} + T_{90}$$

ASTM has adopted DI as one of the standard requirements for good quality gasoline. DI should be less than 597°C (1250 °F) during warm weather and less than 569°C (1200°F) in cold weather. It has been shown that gasolines blended with ethanol do not follow this relationship. For fuels having high values of DI, the presence of ethanol degrades performance relative to non-oxygenated fuels, even at equal levels of T_{10}, T_{50} and T_{90} and an offset is required (21). The exact magnitude of the offset and the form of the equation have not been resolved, and ASTM still recommends using the equation shown above.

Icing. At temperatures within 5°C of freezing and under conditions of high humidity, ice can form in the intake system of vehicles with carburetors or throttle body fuel injectors. When the gasoline in these systems evaporates, it cools the incoming air because of the latent heat of vaporization. If the air is near its saturation point, ice crystals can form on the throttle plate, on the choke plate, or in the venturi throat. The ice can cause rough idle if it accumulates around the edges of the throttle plate when it is nearly closed. In the extreme, ice can clog the carburetor jets and stall the car completely. After the car is fully warmed-up there is generally enough heat in the intake system to prevent any ice buildup. The universal adoption of port fuel injection has eliminated this concern from today's cars.

Back-End Volatility. The portion of the gasoline that boils above 150°C is referred to as the back end. Molecules in this region have high energy density and provide a significant contribution to fuel economy. Too much material in this boiling range, however, can cause problems. This material is hard to volatilize and when the engine is cold, tends to accumulate on the walls of the cylinder. From there it can be washed into the oil sump and dilute the oil. Generally, as the engine heats up this material evaporates. However, if there are too many back ends in the gasoline, then not all may boil off and the performance of the

Table 4. **ASTM Vapor Pressure and Distillation Requirements**

Class	Vapor pressure, max, kPa	T_{10}, max, °C	T_{50}, °C	T_{90}, max, °C	End point, max, °C	Driveability index, max, °C
AA	54	70	77–121	190	225	597
A	62	70	77–121	190	225	597
B	69	65	77–118	190	225	591
C	79	60	77–116	185	225	586
D	93	55	66–113	185	225	580
E	103	50	66–110	185	225	569

lubricant may be degraded. Very heavy molecules, such as those having more than 12 carbon atoms, may contribute to combustion chamber deposits. Condensed ring aromatics are particularly strong contributors to these deposits (22).

Vehicle volatility requirements are a strong function of ambient temperatures. As described above, at any given ambient temperature, volatility should be within a certain range. Too high and vehicles may experience vapor lock. Too low and vehicles may experience hard starting and poor driveability. ASTM has defined six volatility classes for good driveability and six classes for vapor lock protection. These specifications are shown in Tables 4 and 5 respectively.

Each month, each state is assigned a class from Table 4 depending on the low temperatures experienced, and a class from Table 5 depending on historical high temperatures. Some states, because of widely varying ambient conditions may contain two or more areas. Together, these two ratings define the volatility range for good gasolines over the course of a year.

Cleanliness. Good gasoline must be both chemically and physically clean. Chemical cleanliness means that it does not contain nor react under conditions of storage and use to form unwanted by-products such as gums, sludge, and deposits. Chemical cleanliness is assured by controlling the hydrocarbon composition and by appropriate additives. Physical cleanliness means that there are no undissolved solids or large amounts of free water in the gasoline.

After production in the refinery, gasoline may undergo two types of oxidative degradation. The first occurs under ambient temperature conditions and

Table 5. **ASTM Vapor Lock Protection Requirements**

	Vapor liquid ratio	
Vapor lock protection class	Test temperature, °C	V/L, max
1	60	20
2	56	20
3	51	20
4	47	20
5	41	20
6	35	20

long periods of time, as long as six months, and is reflected in storage stability. The second has an impact on high temperature stability and is a phenomenon of the high temperatures and short residence times encountered as the fuel makes its way through the vehicle intake system. Both mechanisms share some similar chemical features in that they involve oxidation of fuel compounds and free-radical polymerization to form high molecular weight gums. The gums and gum precursors formed under storage conditions can lead to damaging deposits in fuel injectors or intake valves.

Compounds associated with poor stability are olefins in general and conjugated diolefins in particular. A compound such as 1,3-cyclopentadiene is known to be particularly detrimental. Compounds having poor stability can be produced in cracking processes such as thermal cracking, including visbreaking and steam cracking, and catalytic cracking. The presence of compounds such as sulfur and nitrogen can also degrade stability and promote gum formation. Vehicle manufacturers know that copper promotes oxidation of the fuel and are careful to minimize the use of copper in the fuel system materials.

A number of laboratory tests are used to predict chemical stability. The amount of existent gum in a gasoline is determined by ASTM D 381. This method involves evaporating a sample by a jet of heated air. The residue is weighed, solubles are extracted with n-heptane, and the sample is reweighed. The total is called unwashed gum and the insoluble portion is called solvent-washed gum. ASTM D 4814 specifies that gasoline should contain less than 5 mg/100 mL of solvent-washed gum. Most gasolines contain less than 3 mg/100 mL.

Although ASTM D 381 measures the gum existing in gasoline at a particular point in time, it does not indicate how much more might be formed during storage at the refinery, during various modes of transportation, in service station tanks, or in vehicle tanks. The oxidative stability test (ASTM D 525) was developed to provide a rapid means of predicting future gum formation. This method consists of placing a sample of the gasoline in a bomb, pressurizing it to 690 kPa (100 psi) with oxygen, and maintaining it at a temperature of 100°C. The pressure inside the bomb is monitored continuously. The oxygen reacts with the gasoline slowly at first, but eventually the pressure drops sharply, 14 kPa (2 psi) or more within a 15 minute interval, indicating a breakpoint. The time from the start of the test to the breakpoint is the induction period and is a measure of the oxidative stability of the gasoline. ASTM D 4814 specifies that gasoline induction period must exceed 240 minutes, although most good gasolines have induction periods in excess of 960 minutes, the duration of the test.

Another ASTM test method, Potential Gum (D 873), combines the existent gum and the oxidation stability tests to measure potential gum. A sample of gasoline is subjected to the oxidation stability test for 960 min, filtered to remove particulates, and then subjected to an existent gum test. The potential gum is expressed as the total (unwashed) gum in this test.

Other tests to predict stability of gasoline have been developed and reported in the literature. One, developed by the U.S. military, stores gasoline at elevated (43°C) temperatures for up to 12 weeks and measures existent gum at the end of that period (23). Another measures existent gum in the presence of copper. The copper catalyzes oxidation and may be a better estimator of the stability of gasoline at high temperature/low residence time conditions.

Laboratory simulation tests have been developed which attempt to provide a better simulation of engine conditions than the analytical tests for predicting high temperature stability and intake system deposits, especially for gasolines containing additives. A test rig has been described (24,25) which could be used in a laboratory to predict the deposits formed in a carburetor and on intake valves. Such a test could be used for certification of fuels or for comparing the potency of competing additives. Nevertheless, these tests have not proven to be accurate measures of the deposit forming tendencies of fuels, and vehicle tests must always be carried out.

In summary, a number of tests are used to predict the chemical stability of gasolines. Although storage stability may be reasonably well predicted by laboratory tests, no test has been developed to predict deposit forming tendencies. This may be a reflection of the various regimes that the fuel undergoes between production and combustion. Even in the intake system itself, the time/temperature history of a fuel in a fuel injector is much different than it is on an intake valve. There is no *a priori* reason why one test should be expected to correlate with all of these cases. For this reason the best tests are not short laboratory tests but long expensive ones such as long-term storage, and engine/vehicle-based deposit tests for fuel injector and intake valve deposit formation. Much more fundamental work on the mechanisms of deposit formation must be carried out before short tests can be expected to be successful.

Other Requirements. There are a number of other specific features that must be present (or absent) in gasoline. Some of these are achieved by blending or manufacturing; others are achieved through the use of additives. Sulfur should not be present as foul smelling mercaptans. The gasoline should not promote rust in pipeline, service station tanks, or vehicle metals. It should be clear and bright in appearance and should not pick up water either as a haze or as an emulsion. Free water in gasoline contributes to rust and corrosion. Gasoline should not contain more than trace amounts of carbonyls which can dissolve elastomeric seals and diaphragms, nor should it contain phosphorus bearing additives which can damage sensitive catalytic converters.

2.2. Manufacture. Crude oil can be easily separated into its principal products, i.e., gasoline, distillate fuels, and residual fuels, by simple distillation. However, neither the amounts nor quality of these natural products matches demand. The refining industry has devoted considerable research and engineering effort as well as financial resources to convert naturally occurring molecules into acceptable fuels. Industry's main challenge has been to devise new ways to meet the tremendous demand for gasoline without, at the same time, overproducing other petroleum products.

Distillation. Petroleum refining begins with the distillation of crude oil into a number of different fractions. In many cases, two distillations are carried out in units called pipestills. The first is at atmospheric pressure and temperatures up to 400°C. The second distillation is carried out at reduced pressure and fractionates the heaviest material from the atmospheric pipestill. Table 6 shows typical boiling ranges for the various crude oil fractions and typical yields from Arab Light, a common crude oil. The yield and properties of these straight-run or virgin fractions are a function of the type of crude oil being distilled. Virgin naphtha can be used as gasoline, except that its octane value is very low

Table 6. **Typical Properties of Crude Oil Fractions**

Fraction	Boiling range, °C	Yield from crude, %
gas	<0	<1
light virgin naphtha	0–100	
heavy virgin naphtha	100–200	18 (L + H)
gas oil/kerosene	200–400	33
residue	>400	48

(78 RON/75 MON). Whereas the potential yield of gasoline directly from crude oil is less than 20%, the demand is about 50%. The heavy material must be converted to lighter material and the octane of many of the existing streams improved by changing chemical composition.

Catalytic Cracking. Although it has long been known that heating crude oil fractions could break or crack the compounds into smaller molecules, the development of suitable catalysts and processing designs has made catalytic cracking the premier refinery process for changing the molecular structure of the crude (see CATALYSIS). Catalytic cracking generates higher yields than thermal cracking as well as superior quality products. Over 50% of the gasoline in the United States is obtained by catalytic cracking which uses a fluidized bed of powdered or small diameter catalysts that are continuously regenerated in an adjacent vessel called a regenerator (see FLUID CATALYTIC CRACKING (FCC) UNITS, REGENERATION; FLUIDIZATION). The fluidized-bed catalytic cracking (FCC) process was first commercialized in 1942 by Standard Oil Co. (New Jersey) at its Baton Rouge refinery (26) using powdered silica/alumina as a catalyst. Fluidized beds offered the ability to use powdered, high surface area catalysts, to operate continuously, to regenerate easily, and to use short contact times which increased yield and selectivity. Since 1942, many improvements have been made in process design, catalyst formulation, and the ability to handle heavier feeds (27–29). Today's catalysts are zeolites having highly controlled pore size and surface area (see MOLECULAR SIEVES).

The principal class of reactions in the FCC process converts high boiling, low octane normal paraffins to lower boiling, higher octane olefins, naphthenes (cycloparaffins), and aromatics. FCC naphtha is almost always fractionated into two or three streams. Typical properties are shown in Table 7. Properties of

Table 7. **Typical Properties of FCC Naphtha**

Property	Light FCC naphtha	Intermediate FCC naphtha	Heavy FCC naphtha
boiling range, °C	<105	105–160	160–220
RON	91	88	91
MON	79	77	81
aromatics, vol%	10	35	65
olefins, vol%	60	20	15

specific streams depend on the catalyst, design and operating conditions of the unit, and the crude properties.

Two undesirable aspects of FCC naphtha quality are that it may contain unacceptably high amounts of foul smelling mercaptans, and that its thermal stability may be too low. Mercaptans are usually found in the light FCC naphtha and may be removed or converted to sulfides and disulfides by a sweetening process such as Merox, developed by UOP. Thermal stability is improved in sweetening processes through removal of cresylic and naphthenic acids. It may be further improved by clay treating and by addition of oxidation inhibitors such as phenylene diamine.

Thermal Cracking. Certain cracking conversion processes are carried out without catalysts. Heavy residuum streams in the refinery can be cracked thermally to produce coke and a mixture of lighter products. If naphtha is produced, it may require extensive treating before it can be used directly in gasoline or used as feed to other processes. Depending on the specific process conditions and design these processes are known as delayed coking, visbreaking , Fluid Coking, and Flexicoking (the last two developed by Exxon). Heavy distillate may also be thermally cracked using high ($\sim$800°C) temperature steam. This process, steam cracking, is used to generate olefins for use in chemicals plants, but also generates material in the naphtha range which, if the quality is appropriate, may be used in gasoline.

Reforming. Catalytic reforming is a process to increase the octane of gasoline components. The feed to a reforming process is naphtha (usually virgin naphtha) boiling in the 80–210°C range. The catalysts are platinum on alumina, normally with small amounts of other metals such as rhenium. Because the catalysts contain noble metals, the feed must have very low levels of sulfur, nitrogen, and heavy metals such as lead and arsenic. Reactors may operate in continuous or semicontinuous mode, the difference being the method in which the catalyst is regenerated. Various designs have been developed by companies such as UOP (Platforming and CCR), Exxon (Powerforming), and Amoco (Ultraforming).

Depending on the catalysts and operating conditions, the following types of reactions occur to a greater or lesser extent: (*1*) heavy paraffins lose hydrogen and form aromatic rings; (*2*) cycloparaffins lose hydrogen to form corresponding aromatics; (*3*) straight-chain paraffins rearrange to form isomers; and (*4*) heavy paraffins are hydrocracked to form lighter paraffins.

Reformers generate highly aromatic, high octane product streams, and a great deal of hydrogen (qv). Reformate can have RON values over 100 and MON values of 90. The hydrogen, which can be used to improve the quality of many other refinery streams, is an extremely valuable product of the reformer.

Some of the negative aspects of reformate are production of benzene, polynuclear or multiring aromatics (PNAs), and light gas (C_1–C_4) (see also BTX PROCESSING). Benzene is a recognized carcinogen and its concentration in gasoline is regulated, whereas PNAs can contribute to combustion chamber deposits. PNAs may be removed by distilling the whole reformate and discarding the heaviest fractions.

Alkylation. Alkylation (qv) is the chemical combination of two light hydrocarbon molecules to form a heavier one and involves the reaction of butenes and butanes in the presence of a strong acid catalyst such as sulfuric or hydrofluoric acid. The product is a heavier multibranched isoparaffin. Propene and the various pentenes may also be used, to produce C_7 or C_9 isoparaffins, respectively. Process designers need to be careful not to let three molecules combine to form C_{12} molecules because these have too high a molecular weight and probably would contribute to poor combustion and higher emissions. Octane numbers for alkylate are usually above 95 for both RON and MON, and the reaction has the effect of lowering the RVP of the available pool, a plus when refiners are trying to reduce it. The principal competitors to alkylation are the various etherification processes which also use C_4 and C_5 olefins as feeds. As a result of environmental concerns associated with use of ethers in gasoline, alkylation is becoming a more desirable process.

There are environmental concerns over the use of HF catalyst. Although the refining industry has taken steps to reduce the likelihood of an accidental release and to minimize the environmental impact in the event of a release, most new units use sulfuric acid catalysts.

Isomerization. Isomerization is a catalytic process which converts normal paraffins to isoparaffins. The feed is usually light virgin naphtha and the catalyst platinum on an alumina or zeolite base. Octanes may be increased by over 30 numbers when normal pentane and normal hexane are isomerized. Another beneficial reaction that occurs is that any benzene in the feed is converted to cyclohexane. Although isomerization produces high quality blendstocks, it is also used to produce feeds for alkylation and etherification processes. Normal butane, which is generally in excess in the refinery slate because of RVP concerns, can be isomerized and then converted to alkylate or to methyl *tert*-butyl ether (MTBE) with a small increase in octane and a large decrease in RVP.

Hydrogen Processing. Hydrogen is probably the most valuable refinery chemical in terms of its ability to improve the quality of refinery streams. It can be used to remove unwanted species such as sulfur and nitrogen from gasoline and diesel. Hydrogen treating improves the ability to resist oxidative degradation and reduces the carbon-forming potential of diesel fuels. Under more severe conditions and with the proper catalysts, hydrogen can saturate olefinic and aromatic bonds. Modern desulfurization process which rely on hydrogen are designed to remove sulfur and avoid unwanted reactions which increase hydrogen consumption and can lower octane by saturating olefins and aromatics. The largest producer of hydrogen in a typical refinery is the naphtha reformer, but hydrogen can also be produced by reforming methane into CO_2, CO, and H_2.

Blending Agents. Blending agents are components of gasoline that are used at levels up to 20% and which are not natural components of crude oil. As of this writing, all blending agents are oxygenated compounds such as ethers (qv) and alcohols and are used for one or more of a variety of reasons, including to increase the octane of the fuel, to reduce vehicle emissions, to reduce dependency on imported crude oil, and/or to reduce emissions of greenhouse gases by using renewable resources.

Ethers, such as MTBE and methyl *tert*-amyl ether (TAME), are made by a catalytic process from methanol (qv) and the corresponding isomeric olefin. These ethers have excellent octane values and compete on an economic basis with alkylation for inclusion in gasoline. Another ether, ethyl *tert*-butyl ether

(ETBE) is made from ethanol (qv) and isobutylene (see BUTYLENES). The cost and economic driving forces to use ETBE vs MTBE or TAME are a function of the raw material costs and any tax incentives that may be provided because of the ethanol that is used to produce it. In the United States, MTBE has been found in groundwater and drinking water supplies, where it imparts a noticeable taste and smell at levels as low as 10 ppb. For this and other reasons, MTBE has been banned in California, New York and Connecticut. Consequently, the use of MTBE in gasoline is expected to decline.

Alcohols such as methanol, ethanol, and *tert*-butyl alcohol [75-64-9] (TBA) $C_4H_{10}O$, have also been used as gasoline blending agents. The only alcohol used in large volumes is biomass-derived ethanol (see CHEMURGY; BIOMASS ENERGY). When ethanol is used as a gasoline blending agent at a level of 10 vol%, the mixture is known as gasohol. Gasohol actually contains only 9.5 vol% pure ethanol because the ethanol must be denatured using 5% unleaded gasoline before it can legally be shipped anywhere. As of this writing, gasohol receives a 5.2 ¢/gal (1.4 ¢/L) federal tax subsidy in the United States. Some states, mostly farm states, also provide additional tax rebates for blenders of ethanol. These incentives significantly improve the economics of ethanol use.

Ethanol gasoline mixtures have a tendency to separate into two phases in the presence of water and ethanol is corrosive in its own right. Therefore, pipeline companies do not allow ethanol blends to be transported through the normal pipeline distribution system (see PIPELINES). Denatured ethanol is transported in trucks, barges or tank cars and blended at terminals. Ethanol also has significant nonlinearity when blended with hydrocarbons, especially for RVP and volatility. Adding only a few percent ethanol can raise RVP of a blend by approximately 1 psi. In order to achieve a final blend with the desired properties, refiners must prepare a special mixture called an RBOB (Reformulated gasoline Blendstock for Oxygenated Blending). Due to ethanols nonlinear blending characteristics, RBOBs must be prepared for specific ethanol contents (ie, 5.7%, 7.7% or 10%). If used for Federal RFG, refiners must make a hand blend of RBOB and ethanol and measure its properties before shipping the RBOB. For California RFG, refiners may use a mathematical model to predict the properties of fully formulated gasoline containing ethanol.

Despite these limitations, gasohol has achieved a significant market share. In 2002, ethanol production accounted for 1.6% of the total U.S. gasoline supply (30). In large farm states, such as Iowa and Nebraska, gasohol sales were 60% and 38%, respectively, of the total gasoline market (31,32).

According to Section 211 of the Clean Air Act, EPA must approve use of any new blending agent in gasoline. “New” means that the agent is not “substantially similar” to unleaded gasoline used to certify 1974 vehicles. In 1981, EPA ruled that gasolines containing up to 2 wt% oxygen were substantially similar (33). All aliphatic ethers and alcohols could be used, except that methanol had to be blended with equal parts of higher alcohols. In 1991, EPA increased the approved level of oxygenates to 2.7 wt% oxygen for aliphatic ethers and alcohols, except methanol (34). A complete list of allowable oxygenates may be found in the literature (35).

Another factor which must be considered when blending oxygenates is the effect of a large amount of a single component on the volatility and therefore

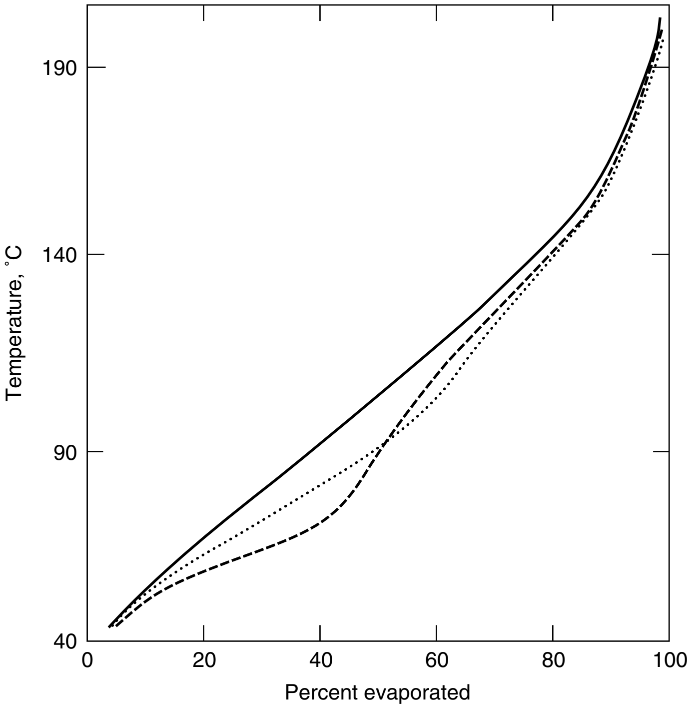

Fig. 3. Distillation curves for (——) nonoxygenated, and oxygenated, ie, (······) 15% MTBE (2.7% oxygen), and (- - -) 10% ethanol (3.7% oxygen), fuels.

the driveability characteristics of the fuel blend. In addition to desired cutpoints, the volatility curve of a good fuel should be smooth and not have any bumps or flat spots. Figure 3 shows the distillation curves for three fuels, one made from hydrocarbons, one containing 15% MTBE, and one containing 10% ethanol. The oxygenated fuels have distinct flat spots which may cause driveability problems in sensitive vehicles.

Additives. Gasoline additives are used to improve the performance of the fuel either because the hydrocarbon components themselves contain some deficiency or because it is more effective to add a small amount of additive than to change the composition of the gasoline. Lead antiknock additives were a good case in point. Octane can be increased either by processing steps such as reforming, which requires significant investment and increased operating costs, or by using additives which is considerably less expensive. Additives are added in parts per million levels to distinguish them from blending agents which are added in the percents. Most additives are added at terminals as gasoline is being pumped from storage tanks. Adjustable pumps are used to inject the appropriate amount of additive.

Dyes. Dyes may be added to gasoline to impart color for a number of reasons. Originally, these compounds were used to identify leaded gasoline so that it would not be used for other inappropriate purposes, such as solvents. Dyes can also be used to identify different gasoline grades so that pipeline companies can separate tenders, and so that service stations can easily check that the correct grade was placed in the underground tanks (aq). Dyes are usually based on azo chemistry and are added in concentrations below 10 ppm. Dyes are rarely used in gasoline today and pipelines rely on other measures such as density to separate tenders.

Antioxidants. Antioxidants (qv) are used in gasoline to improve storage stability. Poor storage stability may sometimes be traced to high concentrations of olefins, especially conjugated diolefins. In many cases, an antioxidant is added to the FCC naphtha in the sweetening process. The antioxidant may be added in large enough amounts so that the blended gasoline contains the proper concentration. Antioxidants are almost always one of two chemical types: phenylenediamines or hindered phenols (qv). These were first used in gasoline around 1930 (36) by Universal Oil Products.

Metal Deactivators. Small amounts of metals in gasoline can contribute to enhanced rates of oxidation. Copper is especially potent in this regard. In order to prevent metal catalyzed oxidation, chelating agents (qv) are often added to gasoline. The most commonly used additive is *N,N′*-disalicylidene-1,2-propanediamine [94-91-7], $C_{17}H_{18}N_2O_2$ (37) at concentrations up to 10 ppm. Special care must be taken if any of the refinery streams are treated with a copper-based process. Automobile manufacturers sometimes use higher levels of metal deactivators in factory fill gasoline, because this gasoline may sit in vehicle tanks for a long period of time until the vehicle is sold.

Corrosion Inhibitors. Corrosion-causing free water is almost always present in at least small amounts in all parts of the gasoline distribution system. It can come about when hot, water saturated gasoline cools in storage tanks or pipelines. Salt water is found in ship holds, and rainwater is found in underground tanks. Acidic or caustic water may be carried over inadvertently from various processes in the refinery. Careful monitoring of service station storage tanks is an important part of good operating practice to prevent unwanted water from contaminating customers' vehicle tanks (see CORROSION AND CORROSION CONTROL).

All corrosion inhibitors in use as of this writing are oil-soluble surfactants (qv) which consist of a hydrophobic hydrocarbon backbone and a hydrophilic functional group. Oil-soluble surfactant-type additives were first used in 1946 by the Sinclair Oil Co. (38). Most corrosion inhibitors are carboxylic acids (qv), amines, or amine salts (39), depending on the types of water bottoms encountered in the whole distribution system. The wrong choice of inhibitors can lead to unwanted reactions. For instance, use of an acidic corrosion inhibitor when the water bottoms are caustic can result in the formation of insoluble salts that can plug filters in the distribution system or in customers' vehicles. Because these additives form a strongly adsorbed impervious film at the metal liquid interface, low liquid concentrations are usually adequate. Concentrations typically range up to 5 ppm. In many situations, pipeline companies add their own corrosion inhibitors on top of that added by refiners.

Rust protection is measured using any one of a number of tests: National Association of Corrosion Engineers (NACE) rust test (40), ASTM D 665, and MIL-I-25017 B/C (41). These all involve immersing a steel spindle in a mixture of gasoline and water for a specified time and evaluating the resulting corrosion.

ASTM D 4914 lists the Copper Strip Corrosion Test which protects against the corrosive effects of fuel sulfur on copper.

Antiicing Additives. Additives to control icing are rarely used in the United States because vehicle design changes have made icing problems almost nonexistent.

Detergent Additives. Deposits may build up in those parts of an engine wetted by fuel: fuel injector, intake valves, and the combustion chamber itself. Both fuel and vehicle design contribute to deposit formation. Proper choice of additive or additives can prevent deposit buildup and in some cases can clean up existing deposits. The exact mechanisms of deposit formation are poorly understood. Moreover, the fuel undergoes a different time/temperature history in each location leading to different types of deposits. An additive that is effective in controlling one type of deposit may not work at all, or may even contribute to increased deposits, in another engine location. For instance, solvent oils can be particularly effective in preventing the buildup of intake valve deposits, but too much solvent oil causes excessive combustion chamber deposits and leads to high ORI. Detergents were first developed for carburetors, and the first was introduced by Standard Oil Co. Of California in 1954 (42). Few if any carbureted vehicles have been made since the mid-1980s, and today's vehicles all use fuel injectors to meter the fuel.

Fuel Injector Detergents. Port fuel injectors generally experience temperatures around 100°C. Deposits can accumulate in the small annulus in the tip of the injector through which fuel must flow. As the annulus become plugged, fuel flow becomes erratic, atomization degrades, and control of stoichiometry becomes more difficult. Although well-designed injectors can tolerate plugging levels of up to 30%, variability among injectors can cause problems even at much lower levels. This is because the vehicle computer controls stoichiometry for all cylinders on average. If one cylinder is running rich, then the other cylinders run lean so that average stoichiometry is correct. Even partially plugged injectors lead to poor driveability and higher emissions as well as loss of fuel economy and engine power.

Although the exact chemical mechanism which leads to injector deposits has not been identified, it is generally believed that heavy hydrocarbons oxidize and polymerize during vehicle hot soak. The resulting gums and resins trap other particles present in the crankcase blowby and in the EGR. Olefins and diolefins are known to be significant contributors, whereas the role of sulfur is still unresolved (43–45). Polar compounds have been shown to contribute to injector deposits. In one experiment, a dirty deposit forming fuel was clay filtered and the resulting filtrate had very low deposit-forming tendencies (46).

A number of additives have been developed which not only prevent injector deposits from forming, but which also remove deposits already in place. The best additives can unclog clogged injectors in less than one tankful of gasoline. Polybutene succinimides, polyisobutylene amines, polyether amines, and certain lower molecular weight amines have been shown to be effective injector detergents (43). Phenylenediamine, which is known to improve the oxidative storage stability of gasoline, does not prevent the reactions which lead to fuel injector deposits. Performance of additives in controlling fuel injector deposits is measured using ASTM D 5598. This is a vehicle based test and involves driving a vehicle with a 2.2 L Chrysler turbocharged engine on a dynamometer for 16,000 km and measuring fuel injector flow compared to baseline values.

Intake Valve Detergents. In the mid-1980s some vehicle manufacturers started to experience levels of intake valve deposits which caused driveability degradation, especially before the engine was fully warmed up. These problems were associated with deposit levels lower than those which had caused problems in the past. It has been hypothesized that the deposits act as hydrocarbon sponges, especially during acceleration when the mixture is usually enriched somewhat in order to provide adequate power. If the deposits, because of physical and chemical makeup, absorb some of the extra fuel that is passing by, the vehicle may stumble and hesitate because the mixture is too lean. Cars built to low emission standards generally have the stoichiometry set as lean as possible during startup and warm-up, and any upset which leans out the mixture even further is not well tolerated.

Intake Valve Deposits (IVD). IVD have been studied extensively and a number of vehicle design and fuel factors have been determined which are principal contributors. As for other deposit-forming problems, the mechanism of deposit formation is not known in much detail, but the broad outlines are fairly well understood. The primary difference between injector deposits and intake valve deposits is the temperature regime. Intake valves generally operate at a temperature as high as 300°C (47), much higher than injectors. The hot soak portion of the driving cycle is not as important for development of IVD as it is for injector deposits. Also, there is a small but constant flow of lubricating oil down the stem of the intake valve which may influence deposit formation.

Vehicle factors that contribute to IVD are typically related to whether or not the valve is kept wet by liquid gasoline during operation. Design factors which encourage wetting of the valve tend to minimize deposits. Valve rotation, which rotates the valves slightly on each cycle, also tends to reduce deposits. Valves that do not rotate develop deposits on the back side which sees little fuel from the injectors. Oil flow down the valves can either help or hurt. If the oil flow is too low, the valve may stay dry, whereas oil flow that is too high encourages buildup of oil related deposits. Injector spray pattern is also important. An even, continuous spray is the best for minimizing deposits, whereas intermittent injectors tend to promote higher deposit levels.

Fuel factors which contribute to IVD have been shown to include olefins (48,49), alcohols, and cracked stocks (50).

Additive packages have been developed that do an excellent job of preventing IVD. The key to effective operation is to keep the valve wet so that the additive can prevent deposit buildup. Most packages include a combination of detergent/dispersant and a carrier oil. If no carrier oil is present, then the fuel may evaporate off the valve too rapidly for the package to be effective. When the valves do not rotate, the portion of the valve which has the highest deposit level is the back side which is not constantly wet.

Additive effectiveness is measured a number of ways, but the most meaningful measures use expensive vehicle testing. ASTM D 5500 involves running a 1985 BMW 318i on the road for 16,000 km, after which the engine head is removed and each valve weighed. No laboratory simulation test has been shown to be a good predictor of IVD and additive effectiveness.

In 1997, EPA implemented detergency requirements for all gasoline sold in the United States. Detergent packages must be certified by gasoline blenders and distributors for nationwide use, for limited geographic use, or for only certain specific blends. Fuels with severe properties (eg, sulfur, aromatics, olefins, T_{90}) must be tested and must demonstrate good detergency performance for fuel injector plugging (ASTM D 5598) and intake valve deposit control (ASTM D 5500).

Combustion Chamber Deposits. As engines age, carbonaceous deposits build up in the combustion chamber-piston crown and top land, head, and valve faces. These deposits, which reach equilibrium after about 20,000 km, are typically 60% carbon, 20% oxygen, 2% nitrogen, and the balance made up of elements from lube oil (51). The heaviest portion of the fuel, especially multi-ring aromatics may be major contributors to the combustion chamber deposits (CCD).

Combustion chamber deposits have extremely good insulating properties and therefore have a number of effects on vehicle operation. Since less heat is rejected to the walls, peak flame temperatures are higher, fuel economy is better, NO_x emissions are higher, and octane number requirements are higher. CCDs are probably the biggest factor contributing to ORI.

Additives used as fuel injector or IVD detergents may also contribute to CCD. Generally, all detergent additives contribute to higher levels of CCD, and their contribution depends on dosage and specific chemistry.

A large study published by the Coordinating Research Council in 2000 examained the effects of CCD on vehicle operation (52). Seven vehicles of each of four models were run for 24,000 km. Emissions were measured at the start and end, and CCD measurements were made at the end of testing. Comparing clean and equilibrated conditions, NO_x and CO_2 emissions, and fuel economy were higher for the equilibrated condition. Two different additives produced higher levels of CCD than nonadditized fuel. NO_x and CO_2 emissions and fuel economy were also higher for the additized fuels. The study could not determine the nature of the relationship between CCD level and emissions or fuel economy.

Development of additives to reduce CCD or to limit CCD growth has been attempted (53), but testing by EPA has failed to substantiate a significant benefit for one additive versus another.

Demulsifiers. Because free water is present in many parts of the distribution system, special care must be taken to prevent emulsions (qv) from forming. Emulsions generally refer to thick oil in water emulsions that are very stable and form a separate phase at the fuel-water interface. Emulsions do not burn very well, and they always carry large quantities of dirt and rust particles with them. These particles plug vehicle fuel filters and cause a car to stop running. Haze is a dilute water-in-oil emulsion in which the water droplets are dispersed throughout the gasoline but which does not form a separate phase. Haze and emulsions may form during high shear conditions such as pumping, or during low shear conditions such as sloshing in the hold of a ship or barge. Gasoline without additives does not generally form emulsions, but the use of surfactants to control deposit formation and limit corrosivity can lead to gasoline having very severe emulsion forming behavior. Demulsifiers are highly surface active chemicals or mixtures having limited solubility in both fuel and water (54). The hydrophilic portion may be polyethylene or polypropylene and the hydrophobic portion may be a long-chain alkylphenol or alcohol. The specific demulsifiers chosen depend on the base gasoline, the rest of the additive package, and the type of water encountered in the distribution system. Demulsifiers may have to work for water bottoms that range from pure rainwater, to salty seawater, to caustic water bottoms (see DISPERSANTS).

In addition to ASTM D 1094, there are a number of widely used industry tests to measure the water handling properties of gasoline. One uses a Waring Blender to simulate high shear (54), whereas another uses a wrist action shaker to simulate mild shear conditions (55).

2.3. Blending and Distribution. When blending gasoline from its components, refinery operators must balance a number of factors in the most economical way. First, the components must be used at the same rate at which these are produced or else the refinery either runs out of material or drowns in excess components. Secondly, each gasoline fuel grade must be produced to the specifications set by marketers and regulators. The specifications should not be exceeded in a way which increases manufacturing cost. Third, blend targets must take into account the fact that the gasoline might not be sold immediately and may travel in pipelines, barges, or tankers and then sit in a distribution terminal. The time between production in the refinery and sale to the customer can be as long as one month. Finally, since all testing has a certain amount of variability, the blender must decide how much margin or "giveaway" to build in to his targets. A large margin is costly but ensures that if a customer tests quality at the time of transfer, or if a regulator checks compliance with regulations, the fuel will likely meet standards. Conversely, with a small margin, the blender runs the risk that a retest of the fuel will show it to be out of specifications. Procedures for adjudicating these kinds of product quality disputes are defined in ASTM D 3244.

Most refineries accomplish the difficult task of planning and executing blending through the use of sophisticated linear programming algorithms. The linear programs are run in a few different time scales ranging from weekly to yearly to help refineries plan their seasonal operations. In the winter, gasoline demand is down and heating oil demand is up; in the summer, gasoline demand is at its peak.

Many gasoline properties, especially octane and RVP, do not blend linearly. Whereas the volatility properties of blends can be well approximated using nonideal properties, it has not been possible to predict the octane values of blends from first principles. It is known that when various refinery streams are blended together, the octane of the blend is usually different from the volume weighted average octane of the individual components. This deviation can be either positive or negative. For instance, blending alkylate and reformate almost always results in an octane number that is lower than the weighted average of the individual components. This is known as an octane blending debit. Likewise, mixing FCC naphtha and virgin naphtha almost always results in a blended octane higher than expected, or an octane blending bonus (56). Experiments using blending agents show that the addition of most agents is nonlinear and depends strongly on the composition of the base gasoline.

Proper prediction of the octane of refinery blends is important because octane has traditionally been one of the most expensive gasoline properties and

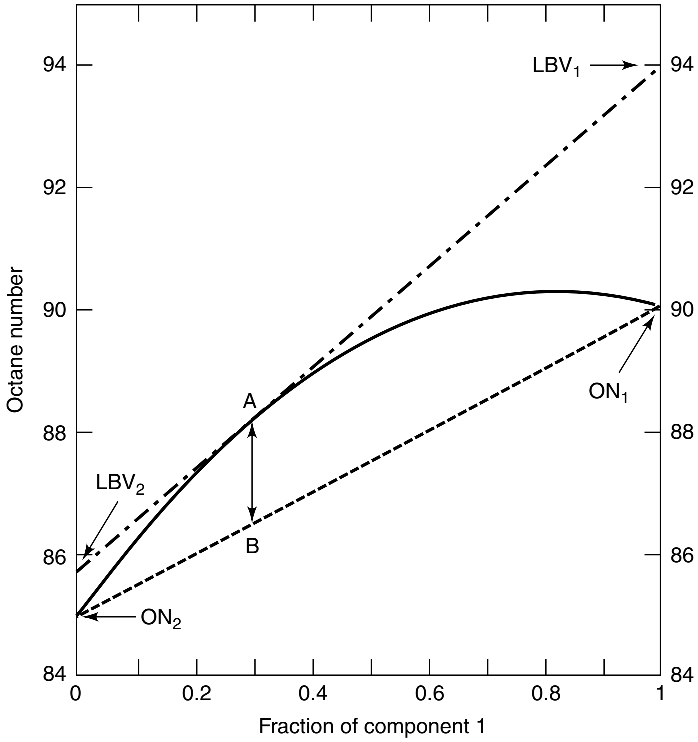

Fig. 4. Octane blending behavior where (—) represents the measured octane response curve, (— · —) the tangent to the curve, and (– – –) the linear connection between the octane number of components 1 and 2. The line AB corresponds to the octane blending bonus of this composition.

raising pool octane often entails significant investment and increased operating costs. Also, it is possible to meet targets for the different grades by properly choosing blend stocks to take advantage of octane bonuses available from the nonlinear blending characteristics.

Blending behavior of a binary mixture may be characterized by a linear blending value (LBV). Figure 4 shows the response curve of a hypothetical two-component mixture. The LBV for each of the components at any composition f_c is defined by the tangent at that point according to the formula.

$$LBV_1 = ON_c + (1 - f_1)\,(dON/df_1)_c$$
$$LBV_2 = ON_c - f_1(dON/df_1)_c$$

where f_1 is the weight fraction of component 1, $(d\mathrm{ON}/df)_c$ is the slope of the blending curve at composition c, and ON_c is the octane number of the blend at composition c.

As can be seen from Figure 4, LBVs for these components are not constant across the ranges of composition. An interaction model has been proposed (57) which assumes that the lack of linearity results from the interaction of pairs of components. An approach which focuses on the difference between the weighted linear average of the components and the actual octane number of the blend (bonus or debit) has also been developed (58). The independent variables in this type of model are statistical functions (averages, variances, etc) of blend properties such as octane, olefins, aromatics, and sulfur. The general statistical problem has been analyzed (59) and the two approaches have been shown to be theoretically similar though computationally different.

Most of the octane blending values reported in the literature use a slight variation on this theoretically sound approach. The composition and octane of the base fuel are assumed to be fixed and the second component is assumed to be added. Using the same nomenclature, the blending octane number (BON) of component 2 is defined as

$$BON_2 = (ON_c - ON_1^* f_1)/f_2$$

The advantage of this definition is that it does not depend on measuring the tangent of the response curve, although the variation in the value of the blending octane number is greater. Typically, BONs are measured at an 80/20 mixture. This technique is also useful when trying to measure the octane of a compound such as butane or methanol that is difficult or impossible to measure in its pure state.

Most refineries develop individual octane blending equations which do a good job of predicting that refinery's blending behavior. In order to use these equations in refinery planning and operations, these may be linearized in a piecewise fashion.

Until the 1960s, most gasoline blending was done in batches. All the components were stored in large tanks, a recipe was defined by a master blender, and an empty tank was filled according to the recipe. After the blend was finished, a sample was sent to the laboratory for testing. If all properties were within specifications, the blend was released. If not, certain components would be added to fix the blend properties. In the extreme, a blend could be downgraded from premium to regular, it could be totally reblended, or it could be sold at a discount to a wholesale customer willing to use off-spec material.

Today, many, if not all of the steps in blending and certifying gasoline have been automated. Computers define preliminary recipes. Although ASTM certification tests are typically laboratory based, some have been adapted and automated for use in the refinery. As a blend is being made in the refinery, samples may be taken automatically as often as every 20 minutes. These samples are fed to special instruments which measure critical properties such as octane and volatility. If the integrated values of the blend are not within specifications, then the automated blenders adjust the recipe.

In a large refinery, an average blend might be 15×10^6 L , having an average flow rate though the blender of 10^6 L/h. When in-line testing is used, a large number of repeat tests conducted on the blend as it is made, and the properties of the blends may be known to a high degree of statistical confidence. The final blends may be pumped directly into a pipeline or a barge.

Sometimes, regulations require that blend properties be measured on a sample of the final blend. In these cases, a sample is taken from the blend tank to the refinery laboratory where it is analyzed again. The single laboratory measurement is then used as the official property of the blend. The outcome of this process is a value that is much less precise than if all the in-line analyzer results would be used.

Gasoline blends are shipped from the refinery to a storage terminal. At the terminal, additives are metered into the gasoline as it is loaded onto tank trucks for shipping to individual service stations. The trucks, which have 40,000 L capacity, have 4–5 compartments so that they can deliver different grades at the same time. Service station tanks are buried underground and have a capacity of 12,000–15,000 L. High volume service stations may have underground tanks as large as 45,000 L. Submerged turbine pumps transfer the gasoline from the tanks to dispensers at the dispensing islands. Tanks have been made of a number of materials, although the most popular today is reinforced fiberglass. As a result of environmental concerns about gasoline leakage from underground tanks, many new installations have double-wall construction with leak detectors between the two walls.

2.4. Fuel Economy.

Fuel economy, typically expressed as distance driven per volume of fuel consumed, i.e., in km/L (mi/gal), is measured over two driving cycles specified by the Federal Test Procedure (60). One cycle simulates city driving and consists of relatively low speed ($\sim$32 km/h) driving, and includes a portion where the car starts after having equilibrated at ambient conditions for 16 hours. The second simulates highway driving conditions and includes higher speeds and fewer starts, stops, and accelerations. The statutory fuel economy standards are based on a harmonic average of the city and highway tests assuming that 45% of distance is accumulated under highway conditions and 55% is accumulated under city driving conditions.

Fuel economy is measured using a carbon balance method calculation. The carbon content of the exhaust is calculated by adding up the carbon monoxide (qv), carbon dioxide (qv), and unburned hydrocarbons (qv) concentrations. Then using the percent carbon in the fuel, a volumetric fuel economy is calculated. If the heating value of the fuel is known, an energy specific fuel economy in units such as km/MJ can be calculated as well.

The most important fuel property in terms of volumetric fuel economy is the volumetric heat content of the fuel. Fuel economy has been shown to respond linearly and with a slope of almost unity to changes in energy content of the fuel. In turn, fuel energy content is most influenced by density and oxygen content. Density is positively correlated with heat content whereas oxygen is negatively correlated. Figure 5 shows the relationship between energy content and fuel economy for a group of twenty 1989 vehicles tested on a wide range of gasolines with and without oxygen (61).

2.5. Environmental Issues.

Gasoline properties discussed up to this point have generally dealt with those properties that contribute to good vehicle operation from a mechanical perspective. Other properties are controlled for environmental reasons and those are discussed in this section. Regulatory authority to control fuel properties for environmental reasons derives from the Clean Air Act and its various amendments.

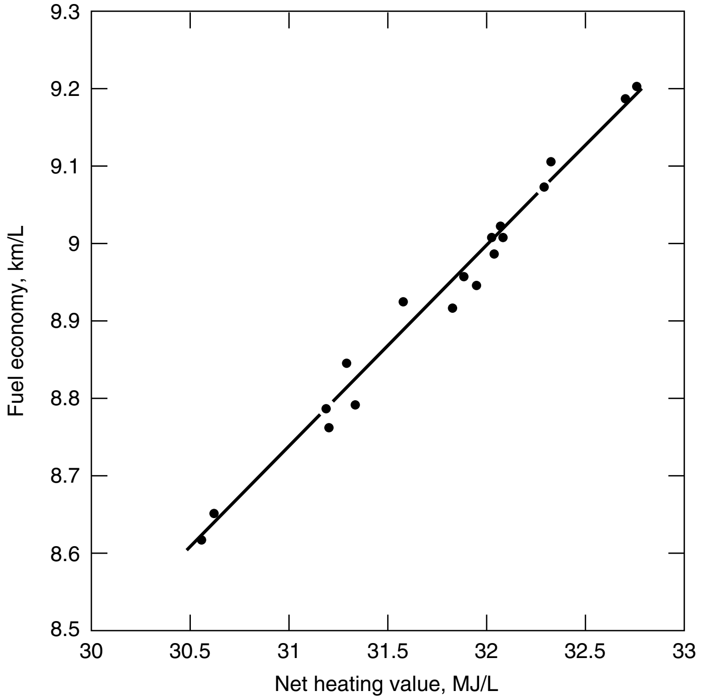

Fig. 5. Fuel economy vs energy content for various fuels. Each data point represents the average of twenty 1989 vehicles. To convert MJ/L to Btu/gal, multiply by 2.78×10^8.

The Clean Air Act directs EPA to set National Ambient Air Quality Standards (NAAQS) for a number of pollutnats such as ozone, CO and NOx, and sets or directs EPA to set vehicle emissions standards and fuel composition standards to help meet these NAAQSs. Because of its especially serious air pollution problems, the state of California is allowed to impose its own strict set of standards under the Clean Air Act.

The first of these standards set by EPA went into effect in 1968 and mandated that the vapors from the vehicle crankcase be routed back through the engine and burned. Since then, the standards have continued to grow stricter. Table 8 shows the federal exhaust emission standards and Table 9 shows the more stringent California standards. A novel feature of the latest federal and California standards is that they must be met by each manufacturer on their sales weighted average. This means that certain vehicles may emit more than others, as long as the average meets the standard. For the federal program, manufacturers must certify vehicles in various bins, which define standards for nonmethane hydrocarbons (NMHC), CO, NO_x and PM, and the sales weighted fleet must meet the NOx average shown in Table 8. In a similar way, the California program defines various emission classes, and sales weighted averages must meet a standard defined in terms of nonmethane organic gases (NMOG). NMOG is very similar to the EPA's NMHC.

The emissions standards have forced changes in vehicle hardware as shown in Table 7. Many of these changes in hardware have resulted in changes in fuel

Table 8. **Federal Light Duty Exhaust Emission Standards (80,000 km)**

	Emissions, g/km[a]			
Year	HC	CO	NO_x	Major hardware changes
pre-control	9.4	56	3.9	
1970	2.5	21		lean combustion
1972	1.8	17		
1973			1.9	exhaust gas recycle
1975	0.94	9.4		oxidation catalysts
1977			1.2	
1980	0.25	4.4		
1981		2.1	0.6	three-way catalysts, oxygen sensors
1994–6	0.16[b]	2.1	0.25	
2001	0.047[c]	2.1	0.12	
2004–07[d]	0.047	2.1	0.031	

[a] To convert to g/mi, multiply by 1.609.

[b] Nonmethane hydrocarbons.

[c] Nonmethane organic gases, the total mass of exhaust hydrocarbon and oxygenated compounds, excluding methane.

[d] Fleet average standards must be met for NO_x, based on emissions in 'bins'. Values shown for NMOG and CO correspond to the Bin 5 standards.

Table 9. **California Light Duty Vehicle Exhaust Emission Standards[a]**

Vehicle type[b]	NMOG, g/km	CO, g/km	NO_x,g/km
LEV	0.047	2.1	0.031
ULEV	0.025	1.1	0.031
SULEV[c]	0.006	0.62	0.012
ZEV	0.0	0.0	0.0
Year			Fleet average NMOG, g/km
1999			0.070
2000			0.045
2001			0.044
2002			0.042
2003			0.039
2004			0.033
2005			0.030
2006			0.029
2007			0.027
2008			0.025
2009			0.024
2010			0.022

[a] Standards at 80,000 km unless shown.

[b] LEV = low emissions vehicle.

ULEV = ultra low emissions vehicle.

SULEV = super low emissions vehicle.

ZEV = zero emissions vehicle.

[c] 192,000 km.

as well. For example, starting in 1975, vehicle manufacturers installed noble metal catalysts in order to meet federal standards and because the catalysts could not tolerate lead, all fuel manufacturers were mandated to sell at least one grade of unleaded gasoline. As demand for unleaded gasoline grew, new processing capacity was required and different blends developed.

In addition to setting standards for exhaust emissions, the government set standards for evaporative emissions. These refer to hydrocarbons that escape from the vehicle when fuel evaporates; while the car is operating (running losses); while it is sitting and not being operated (diurnal emissions), immediately after operation (hot soak); or while it being refueled. In order to control evaporative emissions, auto manufacturers have installed canisters of activated charcoal in their vehicles since 1972. The charcoal traps any hydrocarbon vapors from the fuel tank or from the intake system. During engine operation, the adsorbed hydrocarbons are stripped off the charcoal by a countercurrent air stream and fed into the engine and burned.

Although the charcoal canisters are about 95% effective, fuel volatility still impacts the mass of vapors that break through the canister. Therefore, EPA mandated that starting in the summer of 1992, RVP levels be reduced below the levels specified in ASTM D 4814. Class C regions, generally the northern part of the country, are limited to a maximum RVP of 62 kPa (9.0 psi) vs an ASTM limit of 79 kPa (11 psi), and the southern Class B regions are limited to a maximum RVP of 54 kPa (7.8 psi) vs 69 kPa (9.0 psi) for ASTM.

The Clean Air Act Amendments of 1990 (67) introduced a new concept in emissions reduction: reducing exhaust emissions by controlling the composition of the fuel. Whereas previous regulations had lowered exhaust emissions by setting standards for new vehicles, this law mandated gasoline marketers to change gasoline composition so that emissions from existing vehicles would be reduced. Reduction targets of 15% and at least 20% were set for 1995 and 2000, respectively. Reductions are to be measured against 1990 vehicles and industry average gasoline. The reductions are for hydrocarbons (summer ozone season only), and for air toxics (year round). Air toxics are defined as the sum of the emissions of benzene [71-43-2], 1,3-butadiene [106-99-0], formaldehyde [50-00-0], acetaldehyde [75-07-0], and polycyclic organic material. Reformulated gasoline (RFG) may not result in any increase in NO_x emissions. Additionally, RFG must contain no more than 1% benzene and at least 2% oxygen.

Each refiner has the flexibility to choose the specific formulation to produce based on the economics of the individual refineries. RFG meeting the statutory requirements must be sold in the nine areas of the country which have the worst ozone (qv) problem. In addition, all other areas of the country which exceed the ozone NAAQS may adopt the RFG requirements. In 2003, approximately 30% of the gasoline sold in the United States was subject to RFG rules.

In the winter, the Clean Air Act mandates that gasoline in all areas which exceed the NAAQS for CO must contain at least 2.7% oxygen. This is based on the assumption that adding oxygen to the fuel reduces CO emissions.

Compliance with the RFG regulations is measured by using a formula to calculate the emissions from a given fuel. This formula, the Complex Model, predicts average exhaust and evaporative emissions as a function of gasoline chemical and physical parameters. In anticipation of the need to develop this equation, and because very little data were available, the three domestic auto companies and fourteen petroleum companies formed a joint research program in late 1989 called the Auto/Oil Air Quality Improvement Research Program (AQIRP). This four-year, $40 million program had the objective of "conducting a research and testing program to develop data on potential improvements in vehicle emissions and air quality, primarily ozone, from reformulated gasoline, various other alternative fuels, and developments in vehicle technology" (63).

The program developed a great deal of information on the effects of fuel properties on exhaust and evaporative emissions (64–66). The data collected by AQIRP represent the largest single body of information collected on this subject. Over two thousand individual emission tests were conducted between 1990 and 1992. EPA used this and other data to generate an equation to predict emissions as a function of fuel properties.

Final regulations were published after much consultation with the oil and automotive industries, and with consumer and environmental groups. Specific reduction targets were set for RFG, and gasoline manufacturers were given the option of complying with the regulations on every gallon or on average. In general, if averaging is used, the standard is more severe (1.5% for VOC, NO_x, toxics) and the performance of any one blend may not be too far below the regulatory level (within 2.5% for VOC, NO_x).

Federal RFG and wintertime oxygenated fuels must contain compounds that add oxygen to the fuel (2% and 2.7% by weight respectively). These requirements have been met for the most part by using MTBE and to a lesser extent ethanol. MTBE use has caused concerns because of underground tank leakage and groundwater contamination. Some states have banned MTBE, and where oxygenates are required by federal mandate, ethanol has been used exclusively. There is considerable political pressure to repeal the portion of the CAA and associated regulations that require oxygenate use. Technically, oxygenates have little or no impact on emissions from modern vehicles, and do not reduce either ozone or CO levels in the atmosphere (67).

The state of California has taken a different conceptual approach to reducing emissions through control of gasoline composition. Instead of defining a performance target, ie, 25% reduction, California has defined composition targets which are aimed at achieving emissions reductions. The third round of regulations, known as Phase 3, are shown in Table 10 and took effect on January 1,

Table 10. **California Phase 3 Gasoline Compostion**

		Values for averagers	
Property	Limit per liter	Average	Cap
RVP, kPa[a]	48	NA	50
sulfur, ppm	20	15	40
aromatics, vol%	25	22	35
olefins, vol%	6	4	10
T_{90}, °C	152	146	166
T_{50}, °C	101	95	104
benzene, vol%	0.8	0.7	1.1

[a] To convert kPa to psi, multiply by 0.145.

2004. Gasoline producers must meet these targets on every liter of gasoline. If desired, a company may choose to meet yearly average targets, but these are slightly more severe than the per liter specifications, and the ranges which may be used for averagers are restricted.

In order to provide refiners some flexibility in meeting requirements, California developed the Predictive Model, which defines trade-offs among the specifications, while maintaining equivalent emissions performance. Refiners use the Predictive Model to define alternative specifications for their operation. These alternative specifications, which can be changed as often as desired, are used in place of the values in Table 9. For instance a refiner may choose a lower sulfur level, say 10 ppm, to offset higher olefins, say 9%.

California regulations have been deemed equivalent to the Federal RFG rules and supersede them except for the use of oxygenates which must be used in areas that would otherwise require Federal RFG (Los Angeles, San Diego, and the San Joaquin Valley). Since California has banned use of MTBE and other ethers, ethanol is the only oxygenate used in the state.

In recent years, other government agencies have regulated gasoline specifications and composition. Some examples are:

Area	Controls
Detroit, Mich.	Low RVP
Pittsburgh, Pa.	Low RVP
Atlanta, Ga.	Low RVP, low Sulfur
Birmingham, Ala.	Low RVP, low Sulfur
Phoenix, Ariz.	CA or Federal RFG, oxygen not required
New York State	MTBE banned
Connecticut	MTBE banned

By one count, 20 different sets of formulations or regulations have been defined across the United States. Many of these so-called boutique fuels are sold in only a small geographic area. Distribution of so many different grades through the fungible pipeline and terminal system has the potential to overload the system and to make temporary supply disruptions or shortages more probable in the event of a refinery upset.

Gasoline composition is also regulated in Europe as shown in Table 11. These values were defined by the European parliament after analysis of air quality and fuel effects on automotive emissions.

Gasoline composition regulations are being considered in many other parts of the world as well. The options range from the basic, such as eliminating lead,

Table 11. **European Gasoline Compostion Regulations**

	2000	2005	2009
sulfur, max, ppm	150	50	10
aromatics, max, wt%	42	35	35
benzene, max, wt%	1.0	1.0	1.0
olefins, max, wt%	18	18	18

to full reformulations such as those adopted in the United States and Europe. The choice of appropriate regulations should be based on many factors, including vehicle technology, the status of air quality, and cost effectiveness relative to other emission control steps.

3. Diesel Fuel

As a fuel for internal combustion engines, diesel fuel ranks second only to gasoline. In 2001, total U.S. demand for diesel fuel for transportation was about 150 billion L, about 29% of the demand for gasoline (68). Use of diesel fuel for highway vehicles accounted for 81% of the total, off-highway vehicles for 6%, ships for 5%, locomotives for 7%, and military use for 1% (69). Diesel cars, thought at one time to be very promising, have encountered significant customer resistance in the United States. There are significant obstacles to overcome. Consumers have perceived diesels as noisy, smoky, and hard to start in winter. The fuel economy benefit that diesel engines can offer is not as attractive when gasoline prices are relatively low. Unites States automotive manufacturers are considering diesels as a way to meet corporate average fuel economy standards and still be able to sell large, powerful SUVs. Increased penetration of diesel engines in the light duty market means that they will have to meet exceedingly strict emission standards and will have to compete with gasoline-battery hybrids for those interested in higher fuel economy.

In many countries, diesels engines do not have the negative image that they do in the United States. Furthermore, tax differentials on fuels and vehicles, as well as overall high fuel prices can make diesel economically attractive. In France, for example, diesel engines constituted 56% of new car passenger and light duty truck sales in 2002, vs about 0.1% in the United States.

3.1. Combustion in Diesel Engines. Unlike the spark-ignited gasoline engine, the diesel engine, first used by Rudolf Diesel in the 1890s to burn finely powdered coal dust, employs compression ignition. Liquid fuel was employed soon after. Through the action of the pistons, air alone is drawn into the cylinders and compressed. Near the end of the compression stroke, fuel is injected into the cylinder and after a short delay, is ignited by the high temperature generated during compression. The fuel must be finely atomized and well mixed with the air for complete combustion to take place. The ignition delay is useful because it allows the fuel to be injected and mixed before combustion starts. Its length depends largely on the composition of the fuel, and is described by cetane number.

Diesel engines offer a number of advantages over gasoline engines. Diesel engines are able to operate at high (16–22) compression ratios which improves energy efficiency. Because combustion starts at many different sites and there is no flame progressing across the combustion chamber, there are no knock concerns. The engine operates with unthrottled air flow, which also improves efficiency. Because the air flow is unthrottled, changing fuel flow results in a wide range of stoichiometry, always in the lean region. Lean operation also means that HC and CO emissions are generally low for diesels. If too much fuel is fed to the engine to boost power, visible black smoke and soot are emitted.

Diesels also suffer from a number of disadvantages relative to gasoline engines. Diesels are generally hard to start in cold weather. Many engines use glow plugs to heat up the combustion chamber so that the fuel can ignite. It used to be common for heavy-duty diesels to be left running in cold weather because they are so hard to restart. Although diesel engine-out emissions of NO_x are not much different from those of equivalent gasoline engines, diesel engines do not have exhaust catalysts so the tailpipe emissions are much higher. Additionally, diesel engines tend to be heavier and more expensive than gasoline engines of the same power due to the need for more structural strength and more complex fuel system.

In assessing the possible health effects of diesel exhaust, EPA concluded that diesel exhaust is likely to pose a lung cancer hazard to humans (70). Components of diesel exhaust that contribute to this assessment include aldehydes, benzene, 1,3 butadiene polyaromatic hydrocarbons (PAH), nitro-PAH, and particulates. EPA's assessment was not able to quantify the risk, nor was it able to identify the hazards posed by specific components. EPA also pointed out that the data was based on engines built before the mid-1990s. The next generation of diesel engines will be much cleaner and the health impacts are likely to be much lower.

There are two categories of diesel engines: direct injection (DI) and indirect injection (IDI). In DI engines, the fuel is injected directly into the combustion chamber. In IDI engines, there is a small prechamber into which the fuel is injected. The fuel starts to ignite in the prechamber and the hot burning gases are forced out into the main combustion chamber through a small passage. IDI engines may operate at higher speeds and use lower pressure injector systems which tend to be less expensive. Most new engines, both light and heavy duty, use DI designs to take advantage of higher power and better fuel economy.

A new approach to diesel engine design is called Homogeneous Charge Compression Ignition (HCCI). In an HCCI engine, the fuel air mixture is homogeneous as in a spark ignition engine and in contrast to a traditional diesel engine, where there is significant nonhomogeneity. However, the combustion is auto-ignited and takes place very rapidly without a flame front. The stoichiometry of the mixture is lean to keep NO_x emissions low. This type of engine has the potential to have very low emissions as well as high efficiency, and combines the best features of gasoline and diesel engines. A key technical hurdle is to make sure that combustion is smooth and complete even under high speed and high load conditions. The fuel requirements are being developed, and it is possible that the fuel will also fall somewhere between traditional gasoline and diesel properties.

3.2. Requirements for Good Diesel Fuel. Diesel fuel is used in a wide variety of vehicular engines ranging from small passenger cars to large trucks and construction equipment. There are actually three grades of diesel fuel defined in ASTM D 975, the specification for diesel fuels. The first is Grade 1-D, suitable for high speed engines which operate under widely varying conditions of speed and load. Grade 1-D also has excellent low temperature properties. Grade 2-D is a general-purpose diesel suitable for use either in automotive or nonautomotive applications. It can be used in high speed engines involving relatively high loads and uniform speeds. Grade 4-D is much more viscous and is used in low and medium speed engines having sustained loads at substantially constant speed. Most cars and trucks use 2-D, a general-purpose grade. 1-D, a more volatile, lower density, lower aromatic fuel, used in cold weather and in municipal buses. Starting in 1993, EPA has lowered the regulated sulfur level of diesel fuel twice and ASTM has defined two new sets of grades-low sulfur (LSD) and ultra low sulfur (ULSD). These are described in more detail below.

Ignition Quality. The ability of diesel fuel to burn with the proper characteristics is described by its cetane number, a measure of ignition delay. Excessively long ignition delays (low cetane number) cause rough engine operation, misfiring, incomplete combustion, and poor startability. Because the fuel starts to burn later in the cycle, pressure rise is more rapid without increasing the net work from the cycle. Power may be reduced and combustion may be incomplete leading to high emissions if the fuel does not have time to burn in the expansion stroke.

The procedure for measuring the cetane number of diesel fuel (ASTM D 613) is similar to that used for measuring gasoline octane number. Cetane [544-76-3] (*n*-hexadecane), $C_{16}H_{34}$, is defined as having a cetane number of 100; α-methylnaphthalene [90-12-0], $C_{11}H_{10}$, is defined as having a cetane number of 0. 2,2,4,-4,6,8,8-Heptamethylnonane [4390-04-9] (HMN), $C_{16}H_{34}$, which can be produced in high purity, is used as the low reference fuel and has a cetane number of 15. Blends of cetane and HMN represent intermediate ignition qualities according to the formula:

$$\text{cetane number} = \%\ \text{cetane} + 0.15\ (\%\ \text{HMN})$$

The cetane engine is a variable compression single cylinder engine very much like the octane engine. The engine is run at 900 rpm and injection is timed to start at 13° before top dead center (BTDC). The compression ratio is adjusted so that the test fuel starts to ignite at exactly top dead center (TDC), for an ignition delay of 13° or 2.4 ms. Reference fuels are chosen which bracket the sample and the cetane number of the sample is estimated by interpolation between the two reference fuels.

The cetane number of a fuel depends on its hydrocarbon composition. In general, normal paraffins have high cetane numbers, isoparaffins and aromatics have low cetane numbers, and olefins and cycloparaffins fall somewhere in between. Most diesel fuels marketed in the United States have cetane numbers ranging between 40 and 50. Most manufacturers specify a minimum cetane number of 40–45.

Cetane number is difficult to measure experimentally. Therefore, various correlation equations have been developed to predict cetane number from fuel properties. One such equation may be found in ASTM D 4737 to calculate a cetane index (CI). ASTM D 975 allows use of CI as an approximation if cetane numbers are not available.

In an effort to improve the precision and cost of measuring cetane number, ASTM has adopted a laboratory device called IQT (Ignition Quality Tester) as method D 6890. This device measures ignition delay in a constant volume bomb, under carefully controlled conditions. Results are converted to cetane numbers by means of a correlation equation. Compared to the cetane engine, the IQT method is less expensive, more precise and faster. D 6890 has not been approved as an alternative to the cetane engine measurement (ASTM D 613) because the bias between the two tests is not fully understood and characterized.

Cold Temperature Properties. Diesel fuel must be able to be pumped and to flow through all filters and injectors at the lowest temperature that may be encountered in use. When the temperature is lowered, wax molecules in the fuel start to crystallize. This temperature is known as the wax appearance point or cloud point. These temperatures, which are generally the same, are measured by ASTM D 2500 and D 3117, respectively. If the temperature is lowered still further, the fuel gels and does not flow. This is the pour point and is measured by ASTM D 97. These tests measure the ability of a fuel to operate in a diesel engine. Generally, the cloud point of a fuel is 4–6°C above the pour point, although fuels having differences of 11°C are not uncommon. The true operability temperature is somewhere in between the two; cloud point is too high and pour point is too low. Many engine manufacturers recommend fuels having pour points of 6°C below the lowest temperature at which the engine is expected to operate.

Some additives have the ability to lower the pour point without lowering the cloud point. A number of laboratory scale flow tests have been developed to provide a better prediction of cold temperature operability. They include the cold filter plugging point (CFPP), used primarily in Europe, and the low temperature flow test (LTFT), used primarily in the United States. Both tests measure flow through filter materials under controlled conditions of temperature, pressure, etc, and are better predictors of cold temperature performance than either cloud or pour point for additized fuels.

If the fuel temperature is below its pour point, the fuel has difficulty flowing out of the storage tank on the vehicle. Diesel powered vehicles generally do not have in-tank pumps. If, however, the fuel temperature is above its pour point but below its cloud point, the following situation may occur. The engine starts but as operation continues, wax crystals begin to collect on the fuel filter, plugging it after a few minutes and stopping the vehicle totally. Vehicle manufacturers can take a number of steps to minimize these problems. Some are relatively expensive, such as heated filters, tanks, and engine blocks. Others are relatively simple although not as effective. These include making sure that the fuel lines have no kinks or sharp bends in them and routing lines through sheltered locations.

Vehicle testing is the best way to determine low temperature requirements. These tests can be carried out in environmentally controlled facilities under strictly defined conditions or in actual use. Many companies and industry groups carry out customer tests in cold climates such as northern Canada or Finland. ASTM D 975 recognizes that “it is unrealistic to specify low temperature properties that will ensure satisfactory operation at all ambient conditions”. Therefore, it specifies that the purchaser and supplier of fuel should agree on low temperature property requirements at the time of purchase.

Volatility. Volatile light fractions in diesel fuel help to provide easy engine starting but are generally low in cetane number and energy content. Heavy fractions, which have good cetane and energy content, can contribute to deposit formation and hard starting if present in too high concentrations. Desirable quality characteristics are obtained by careful blending of refinery streams. The temperatures at which 10, 50, and 90% of the fuel evaporate in the ASTM D 86 distillation test are used as controls to provide good volatility. In general, most diesel fuels have an initial distillation temperature above 160°C and a 90% point of 290–360°C, depending on fuel grade.

Viscosity. For optimum performance of diesel engine injector pumps, the fuel should have the proper viscosity. Too low viscosity results in excessive injector wear and leakage. Viscosity that is too high may cause poor atomization of the fuel upon injection into the cylinders.

Diesel fuel kinematic viscosity is measured by ASTM D 445, and is reported in units of mm^2/s at 40°C. Desired viscosity is a function of fuel grade and ranges from a minimum of 1.3 mm^2/s for 1-D to a maximum of 24 mm^2/s for 4-D.

Density. The greater the density of diesel fuel, the greater its heat content per unit volume and therefore the greater its power or fuel economy. Because diesel fuel is purchased on a volume basis, density is often stipulated in purchase specifications and measured on delivery. A common measurement of density is API gravity (ASTM D 287), which is measured easily and accurately using calibrated hydrometers. The relationship between specific gravity (SG) and API gravity is

$$^\circ\text{API at } 15.6^\circ\text{C} = (141.5/\text{SG}) - 131.5$$

Flash Point. The flash point of a fuel indicates the temperature below which the fuel can be handled without danger of fire. This is the temperature to which the fuel must be heated to create sufficient vapors above the surface of the liquid that they can be ignited in the presence of an ignition source. The flash point of diesel fuel is measured by ASTM D 93, using a closed-cup Penske-Martens tester. The fuel is heated at a rate of 5.6°C/min and a test flame is introduced into the test chamber at 30 s intervals. The fuel temperature reached when the flame ignites the vapors is called the flash point. Specifications for flash point vary with grade; the lowest value is 38°C for grade 1-D. Controlling flash point is important in order to prevent the vapor space in storage and vehicle tanks from being in the explosive range. Setting the flash point at 38°C protects most storage vessels from exploding.

Carbon Residue. The tendency of a diesel fuel to form carbon deposits in an engine can be roughly predicted by the Ramsbottom Coking Method (ASTM D 524), which determines the amount of carbon residue left after evaporation and chemical decomposition of the fuel at elevated temperatures for a specified length of time. The Ramsbottom method involves heating the last 10% residue of the ASTM distillation at 549°C for 20 minutes. The result is reported as percent carbon on 10% residuum. For use in high speed diesel engines operating over a range of loads and speeds, ASTM specifications call for no more than 0.15% Ramsbottom carbon residue. Because ignition control additives may interfere with the tests without actually leading to deposit formation in the engine, these laboratory tests should be made on fuel before any addition of ignition control agent.

Sulfur. Sulfur in diesel fuel should be kept below set limits for both environmental and operational reasons. Operationally, high levels of sulfur can lead to high levels of corrosion and engine wear owing to emissions of SO_3 that can react with condensed water during start-up to form sulfuric acid. From an environmental perspective, sulfur burns to SO_2 and SO_3, the exact split being a function of temperature and time in the combustion chamber. SO_3 can react with water vapor in the exhaust which can further react to form sulfates, leading to high levels of particulates. Although the SO_3 fraction may be small, diesel fuel has traditionally contained sulfur concentrations as high as 5000 ppm. As particulate emission standards for diesels became more stringent, engine manufacturers made the case that they could not meet the standards unless sulfur levels were reduced. Through negotiations between the Engine Manufacturers Association and API, it was agreed that sulfur content of highway diesel could be reduced, and EPA specified a maximum level of 500 ppm starting in October, 1993. In December 2000, EPA promulgated new emissions standards for diesel engines and concluded that these standards could only be met if diesel fuel for on-road engines were also reduced. Starting in 2006 and phasing in fully by 2010, diesel fuel for on-road engines must have a sulfur level below 15 ppm. Starting in 2010, diesel fuel for nonroad engines, such as farm and construction equipment, must also be below 15 ppm. Manufacturers are expected to target refinery release limits of approximately 8 ppm to take into account the sulfur picked up in pipelines and other parts of the distribution system. This margin may change over time as experience is gained in shipping low sulfur products.

Ash Content. The fuel injectors of diesel engines are designed to very close tolerances and are sensitive to any abrasive material in the fuel. Therefore, the maximum permissible ash content of the fuel is specified. This is measured by ASTM D 482, which consists of burning a small sample of the fuel in a weighed container until all the carbonaceous matter has been consumed. The permissible amount of ash is between 0.01 and 0.1 wt% depending on the grade of diesel. Low speed engines operating at constant speed and load can tolerate higher levels of ash.

Aromatics Content. Aromatic compounds have very poor ignition quality and, although they are not specifically limited in ASTM D 975, there are practical limitations to using high aromatic levels in highway diesel fuel. In the United States, where gasoline demand represents about one-half of the crude barrel, and where heating oil demand is relatively low, there is great pressure to be able to blend aromatic FCC streams into diesel fuel. Average aromatic levels in the United States are about 33%. In addition to having poor fuel quality, aromatics also contribute to exhaust emissions. The federal government began effectively limiting aromatic content to below 40% starting in October, 1993 by specifying a minimum cetane index of 40. California limits aromatic levels below 10% beginning in the same time period, also because of emissions concerns. It is expected that average aromatic levels in ULSD will be lower than current levels because the refinery processes used to reduce sulfur will also saturate some aromatics. The magnitude of this change is difficult to predict.

Stability. Diesel fuel can undergo unwanted oxidation reactions leading to insoluble gums and also to highly colored by-products. Discoloration is believed to be caused by oxidation of pyrroles, phenols, and thiophenols to form quinoid structures (71). Eventually, these colored bodies may increase in molecular weight to form insoluble sludge.

Gums can lead to deposits in critical injector orifices that can degrade atomization and combustion performance of the engine. The chemistry involved in the formation of these gums appears to be similar to that which occurs in gasolines. Stability is measured using ASTM D 2274. In this test, a sample is heated at 95°C for 16 hours while oxygen is bubbled through the liquid. After cooling, the insoluble material is filtered and washed. The amount remaining is reported as gums.

Lubricity. Diesel fuel has traditionally had adequate lubricity to protect fuel pumps and injectors from excessive wear. Changes in equipment and fuel processing have caused concern that lubricity may no longer be adequate. Pressures in modern unit fuel injectors may be as high as 170 MPa (25 kpsi) and tolerances for direct injection equipment have become much tighter. Lower viscosity fuels have poorer lubricity, and processing steps that lower sulfur may also remove trace levels of surface active compounds that provide natural lubricity.

Lubricity is measured in two different tests: ASTM D 6078, the scuffing load ball-on-cylinder evaluator (SLBOCLE); and ASTM D 6079, the high frequency reciprocating rig (HFRR). In response to concerns voiced by engine and equipment manufacturers, ASTM will likely adopt a maximum specification of 520 mm average wear scar in the HFRR test. Fuels which do not meet this specification will have to be additized, either at the refinery or at the terminal.

ASTM specifications for different grades of diesel fuel are summarized in Table 12.

3.3. Diesel Fuel Manufacture. The biggest factors in determining how diesel fuel is blended in a given refinery are the availability of high cetane stocks. In order of decreasing ignition quality, the hydrocarbon types rank in the following order: normal paraffins, olefins, cycloparaffins, branched paraffins, and aromatics. Because straight-run distillates contain the greatest amount of normal paraffins and cycloparaffins and the least amounts of branched paraffins and aromatics, these are the preferred stocks for diesel blending. Cracked stocks, which are relatively rich in aromatics, are less desirable from the standpoint of ignition quality. However, these have high energy density and good cold temperature properties. The amount of cracked material allowable in diesel

Table 12. **Specifications for Diesel Fuel (ASTM D 975)**

	Grade		
Fuel Property	1-D	2-D	4-D
flash point, °C (min.)	38	52	55
T_{90}, °C	288, max	282-338	
kinematic viscosity, mm^2/s	1.3-2.4	1.9-4.1	5.5-24.0
carbon residue, % (max)	0.15	0.35	
ash, % (max)	0.01	0.01	0.10
sulfur, % (max)[a]	0.50	0.50	2.00
cetane number (min)	40	40	30

[a] Sulfur values are for regular grade diesel (RSD). Low sulfur diesel (LSD) has a specification of 0.05%, and ultra low sulfur diesel (ULSD) has a sulfur specification of 0.0015%.

fuel depends largely on the cetane number specification. In the United States, where a high level of cracking is necessary to meet gasoline demand, the large supply of cracked fractions and the relatively small supply of straight-run distillates make substantial use of cracked stocks economically necessary. This has been made possible through the use of cetane improvers to improve cetane and through the use of hydrogenation to improve stability.

Ignition Improvers. In order to meet the increasing demand for diesel fuel and to allow use of blendstocks having good low temperature properties but low cetane number, diesel manufacturers frequently use cetane improvers in the fuel. Cetane improvers work in just the opposite way that antiknock additives do. During the preignition period, the improvers generate free-radical species that promote faster onset of combustion and reduce the ignition delay properties of the base fuel. Various types of chemicals have been shown to be effective, including nitrates and nitrites, nitro and nitroso compounds, and peroxides (71). Alkyl nitrates are by far the most common and are used in concentrations up to 0.3%. Although the effectiveness varies with base fuel composition, 0.1% in a typical fuel would give an increase of five numbers (72).

Stability Improvers. Diesel fuels that contain high amounts of cracked stocks generally have poorer stability than virgin diesel. If the fuel is hydrotreated to remove sulfur, the stability is vastly improved. Traditional antioxidants such as hindered phenols are not particularly effective in preserving color although these still prevent other oxidation reactions. Stabilizers are amines or other nitrogen-containing compounds that prevent sediment formation by interfering with the oxidation reactions that occur between heteroatoms and available oxygen. These act as radical traps and/or peroxide decomposers.

Corrosion Inhibitors. The corrosion inhibitors used in diesel fuel are generally similar to those used in gasoline and, like the latter, produce an effect primarily by surface action. If amine additives are used for detergency, these may provide some corrosion protection as well.

Detergent Additives. Diesel engine deposits are most troublesome in the fuel delivery system, ie, the fuel pump and both fuel side and combustion side of the injectors. Small clearances and high pressures mean that even small amounts of deposits have the potential to cause maldistribution and poor atomization in the combustion chamber. The same types of additives used in gasoline are used in diesel fuel. Low molecular weight amines can also provide some corrosion inhibition as well as some color stabilization. Whereas detergents have been shown to be effective in certain tests, the benefit in widespread use is not fully agreed upon (73).

Cold Flow Improvers. The cold flow properties of diesel fuel may be improved by the use of additives or blending agents. As is the case for gasoline, additives are materials present in low concentrations (ppm), whereas blending agents are present in levels of a few percent or more. Blending agents work by diluting the concentration of wax crystal forming paraffins to a point below which these paraffins are no longer a problem. Kerosene and grade 1-D diesel fuel may be used as effective diluents. Gasoline, which also improves cold flow properties, is unsafe and dangerous to use as a blending agent because it can drastically lower the flash point of the mixture and lead to poor lubricity.

Additives are often the most economical way to improve the cold flow properties of middle distillates. These additives have been called by a number of different names including wax crystal modifiers, mid-distillate flow improvers, and wax antisettling additives. All additives work by modifying the crystallization process in some way. Some change the shape of the wax crystals so that the crystals are less likely to plug fuel system filters. Others work by promoting nucleation of many small crystals instead of the growth of relatively few large crystals (74). Various types of chemistry have been shown to be effective in improving low temperature flow properties of diesel fuels. Examples are ethylene–vinyl ester copolymers, chlorinated hydrocarbons, and polyolefins. The exact nature of most commercially available additives is proprietary. Treatment rates and the specific additive formulation used are a strong function of the fuel composition and depend in large part on the distribution of molecular weights of the normal paraffins in the fuel and the concentration of high molecular weight paraffins (75). Fuels having a wide distribution of molecular weights are the most responsive to flow improver additives.

Three types of cold flow additives have been described (76). The first are pour point depressants, which are primarily low molecular weight ethylene–vinyl ester copolymers. These work by cocrystallizing with the paraffin wax and preventing further paraffin addition to existing crystals. The second type of additive is the cloud point depressant (CPD). CPDs are low molecular weight polymers where the paraffin segments have been designed to interact with the paraffins in the fuel to delay the onset of crystallization. The third type of additive is called an operability additive (OA). OAs are multicomponent additives optimized for given fuel properties and show an improvement in the cold filter plugging point and low temperature flow tests as well as lowering the pour point.

Lubricity Improvers. Lubricity performance of modern low sulfur, low aromatic diesel fuel in modern diesel engines is a concern. Some of these concerns surfqaced in Sweden with the introduction of Swedish Class 1 and Class 2 diesel in the early 1990s. A number of additives are available which can improve lubricity as measured in ASTM D 7078 mand D 6079 at concentrations of 100–200 ppm. Use of fatty acid methyl esters has also been shown to improve lubricity.

Dyes. Azo type dyes are fairly common in diesel fuel, and red dye is used to identify fuel for nonroad applications, which is not subject to highway taxes. This practice makes it easy to identify cheating and to enforce tax regulations. Any red diesel found in nonroad equipment is evidence of cheating. Clear diesel found in nonroad equipment usually means that on-road fuel was downgraded at some point in the distribution system.

Antifoamants. When diesel fuel is splashed into tanks, it can foam up to such an extent that the foam can splash onto the customer or onto the ground. Antifoamants are silicon based additives that reduce foaming tendnecies so that a high fueling rate can be maintained. Treat rates are usually below 30 ppm.

Oxygenates. Oxygenated materials have been considered for addition to diesel fuels for the same reasons these compounds are added to gasoline. Putting oxygen in the fuel should lead to better combustion and reduced emissions of CO and, more importantly, particulates. However, use of oxygenates has also been shown to increase emissions of nitrogen oxides. A number of different oxygenates have been tested, including esters; ethers (qv); and alcohols. The most common oxygenates used or advocated for use in diesel fuel are fatty acid methyl esters (FAME). FAME can be made from vegetable oils such as soy (SOME), or rapeseed oil (RSME), or from animal fat, such as cooking grease. The term biodiesel generally represents FAME made from a renewable oil. If pure biodiesel is used, it is called B100. Other concentrations, such as B5 or B20, can be used too.

FAME has a number of advantages. It has a high cetane number and good lubricity. Emissions of hydrocarbons, and particulates are significantly lower than standard diesel fuel. Finally, use of biodiesel can reduce emissions of greenhouse gases.

FAME also has a number of disadvantages. Emissions of NO_x are higher than commercial diesel. Cold flow and stability may also be worse.

Generally, engine manufacturers have supported FAME use at levels below 5%, if the material meets the requirements of ASTM D 975 and if the ester meets the requirements of ASTM D 6751. Use of biodiesel has been limited primarily because of its high cost.

3.4. Diesel Environmental Regulations. Emission standards have been set for heavy-duty vehicles in much the same manner as they have been set for gasoline engines. Because heavy-duty vehicles are primarily diesels, the focus is on diesel engine emissions. Standards have been written in units of grams per brake-horsepower-hour ($\text{g/bhph} = \text{g/kW} \cdot \text{h} \times 1.34$), which normalize the emissions according to the total energy output of an engine over the specified driving cycle. In contrast to light-duty vehicle testing where testing is carried out on the total vehicle, heavy-duty engines are certified in tests on an engine dynamometer. A series of accelerations is carried out and the emissions are measured. Table 13 shows U.S. emissions standards. For heavy-duty engines, the most difficult emissions standards to meet are total particulates and NO_x. When standards were relatively high, they were met by engine redesign without fuel changes. Since 1994, fuel changes have also been specified. Many studies have been published on the interactions between engine design, fuel composition, and emissions, and the conclusions are not always in agreement. It is generally

Table 13. **Federal Heavy-Duty Truck Exhaust Emission Standards, (g/kW · h)**[a]

Year	HC	CO	NO_x	$HC + NO_x$	Particulates
1970	4.89	47.4			
1974		30		11.9	
1979	1.1	18.7		7.5	
1984	0.97	11.6	8.0	3.7	
1985	0.97	11.6	8.0		
1988					0.45
1990			4.5		
1991			3.7		0.19
1994					0.07
1998			3.0		
2007[b]	0.10		0.15		0.007

[a] To convert g/kW · h to g/bhp-hr, multiply by 1.340.

[b] 2007 standards for NO_x phase in over three years.

agreed that sulfur contributes to sulfate particulate emissions and that lowering sulfur helps to meet the particulate standards. Higher aromatics, especially PAHs (polycyclic aromatic hydrocarbons) are known to contribute to organic carbon based particulates. Particulate emissions have also been shown to be affected by fuel density (77). The impact of cetane has been shown to be positive and negative. In older heavy duty engines, higher cetane was generally correlated with lower levels of NOx and particulates. In modern heavy duty engines, this effect seems to be negligible. In modern European light duty diesels, higher cetane can actually increase particulate emissions.

It is also generally agreed that in terms of engine design parameters, there is an inverse relationship between NO_x and particulates. Rapid, complete combustion reduces particulate emissions but also promotes the formation of NO_x. Exhaust gas recycle (EGR), which lowers NOx emissions, generally causes particulate emissions to increase.

It is expected that diesel engine manufacturers will use exhaust aftertreatment devices to meet the NO_x and particulate emissions standards that take effect in 2007–2010. Particulates will likely be controlled by catalyzed traps; NO_x will be controlled either by NO_x reduction catalysts that operate under lean conditions or by catalysts that use a reductant such as urea. In anticipation of these devices, and in anticipation that the devices would only work with extremely low levels of sulfur, EPA enacted the ULSD regulations described above.

California has taken a slightly different approach to diesel fuel composition standards from that of the federal government. In October, 1993, California limited diesel fuel to no more than 10% aromatics and 500 ppm sulfur. Alternative formulations are possible if these are shown to have equivalent NO_x emissions to a base reference fuel. In addition to the specifications that apply to the commercial fuel, other aspects of the reference fuel composition are tightly controlled. The fuel must also have a minimum cetane number of 48 without cetane improvers. Fuel manufacturers test the emissions from proposed alternatives and compare them to the emissions from the reference fuel. For instance, manufacturers may be able to produce higher aromatic fuel if the fuel also has higher cetane number. In 2003, most diesel fuel in California used an alternative formulation. Based on a small sample, average aromatics were 20%, average cetane was 51 and average sulfur was 40 ppm in the Los Angeles area in the Summer of 2003 (78). Starting in 2006, California is adopting the federal sulfur limit of 15 ppm in addition to its other requirements.

In Europe, the European Union has defined diesel composition standards as shown in Table 14.

Table 14. **European Diesel Specifications**

	2000	2005	2009
sulfur, max, ppm	350	50	10
T_{95}, max, °C	360	360	360
cetane number	51	51	51
PNA, max, wt%	11	11	11
density, kg/m^3	845	845	845

4. Alternative Fuels

Alternative fuels fall into two general categories. The first class consists of fuels that are made from sources other than crude oil but that have properties the same as or similar to conventional motor fuels. In this category are fuels made from coal, shale and natural gas through Fischer-Tropsch synthesis. (see FUELS, SYNTHETIC, GASEOUS FUELS). In the second category are fuels that are different from gasoline and diesel fuel and which use redesigned or modified engines. These include compressed natural gas (CNG), liquefied petroleum gas (LPG) and hydrogen. The most probable use of hydrogen would be in fuel cells vehicles, both of which will be discussed elsewhere.

During World War II, Germany developed large-scale production of fuel from coal using Fischer-Tropsch synthesis. In the United States, in the 1970s, interest in producing alternative fuels was generated by upheavals in the price and availability of crude oil. In addition to coal, a great deal of research was carried out to develop processes to develop fuels from oil shale and natural gas.

Production of synthetic fuels from coal, oil shale, and methane involves changing the chemical structure of the raw material, especially the hydrogen–carbon ratio. In coal, the hydrogen–carbon ratio is too low and the molecular weight of the raw material is too high to burn cleanly. Coal can be converted to syngas (CO/H_2) and then converted to liquids via Fischer-Tropsch synthesis. Alternatively, it may be liquefied directly with the addition of hydrogen. Oil shale is retorted in large reactors or *in situ* to convert the solid organic material (kerogen) into a synthetic crude oil. The oil is processed to resemble crude fractions. Methane may be converted to hydrocarbon liquids or to methanol via gasification to syngas (CO/H_2) followed by Fischer-Tropsch reactions. A principal factor in all of these processes is the amount of energy needed to run the process and the disposition of the waste products. In the case of shale oil, the spent rock takes up more volume than the original shale and has to be disposed of in an environmentally safe manner.

Decisions on commercialization depend on a number of factors, including the price of the new energy source relative to the price of crude oil, need for energy self-sufficiency, and environmental considerations. The factors are different for each of the potential sources. In the case of natural gas, conversion to Fischer-Tropsch liquids must compete with the production of liquefied natural gas (LNG). Environmental considerations include pollution from burning the fuel itself, pollution from the whole production cycle, and production of gases that are involved in the enhanced greenhouse effect (see AIR POLLUTION). With the dramatic improvements in the low emissions capability of gasoline vehicles, the incremental improvement offered by some alternative fuels can be very expensive and has tended to limit their introduction. Today, most alternative fuels are being considered for their ability to reduce emissions of greenhouse gases and the desire to reduce dependence on petroleum based fuels.

Fischer-Tropsch liquids made from natural gas (GTL) seem to be the most likely fuel in this category to reach the market. GTL plants can produce a very high quality fuel in the diesel boiling range. Sulfur and aromatics are essentially zero, and cetane numbers can be as high as 75. The most efficient use of this material will probably be as a blendstock in conventional diesel, and not as a fuel in its own right.

4.1. Compressed Natural Gas. Compressed natural gas (CNG), which contains mostly methane, is used in almost 1.5 million passenger cars and light duty trucks worldwide and offers a number of clear environmental advantages. It has a high octane number, has the potential to be clean burning, and is currently shipped through pipelines to many parts of the country. Optimized engines would have high compression ratios to take advantage of methane's high octane number. These vehicles store the CNG in high pressure cylinders made of lightweight spun carbon fiber (see CARBON AND GRAPHITE FIBERS) and use specially designed fuel injectors. Dedicated CNG vehicles are projected to have improved energy efficiency and lower emissions of hydrocarbons, carbon monoxide and carbon dioxide.

Unfortunately, CNG also has a number of disadvantages. The energy density of methane is very low and it cannot be compressed enough to provide equal volumetric energy density to gasoline. Producers of automobiles are faced with either eliminating trunk space to provide equal range or compromising on both range and storage space. New infrastructure would have to be put into place to refuel CNG vehicles. A service station refueling island would could cost \$500,000 or more, and refueling a car would take about 10 minutes. A home compressor capable of overnight refueling would cost anywhere from \$3,000–8,000.

CNG has some potential environmental debits as well. To achieve maximum energy efficiency, CNG vehicles would probably operate on the lean side of stoichiometry, and this makes catalytic control of NO_x difficult. Methane is also a potent contributor to enhanced global warming, being anywhere from 20–50 times worse than CO_2. Exhaust emissions of methane and leaks in the distribution system must be tightly controlled. The exact leakage rate is not well known but estimates range from less than 1% to almost 7%.

In the United States, CNG's initial use is in captive, centrally refueled fleets which require limited range, such as delivery vans, taxis, or school buses. Such vehicle fleets can afford the capital cost of refueling equipment and can tolerate the slightly longer refueling times. Fleet experience with CNG has been somewhat disappointing. CNG trucks and buses cost more than their diesel counterparts and have had poor reliability and high maintenance costs. In order to reduce exhaust emissions, it may make more sense to use a limited budget to purchase new, low emitting diesels, or to retrofit existing diesels with particulate taps.

4.2. Liquefied Petroleum Gas. Liquefied petroleum gas (LPG) is a generally available fuel that is a mixture of mostly propane and butane. The exact proportion depends on marketplace conditions and alternative outlets for the two main components. LPG has a number of advantages over both gasoline and methane. It has a higher energy density than methane, because LPG is a liquid. It is easier starting than gasoline because of its higher vapor pressure. Generally, LPG vehicles vaporize the fuel before it is fed into the engine. In cold weather, if the butane content is too high, the fuel may have trouble vaporizing. The largest problem with LPG is that the supply is not large enough to make a significant dent in the total fuel demand picture.

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